A STUDY OF LASER AND PRESSURE-DRIVEN RESPONSE MEASUREMENTS FOR SOLID PROPELLANTS AT LOW PRESSURE

A Thesis in

Mechanical Engineering

by

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ABSTRACT

This work was part of a larger program aimed at understanding and modeling propellant combustion and its interaction with changes in pressure and velocity in a typical rocket motor. A pressure driven combustion facility was developed and used to measure pressure-coupled amplitude and phase response during combustion of propellant samples at low pressure. Laser-driven experiments were also performed in a different chamber to measure propellant response at atmospheric pressure. A CO₂ laser was used to ignite and sustain combustion during laser and pressure-driven combustion and also served as a source of oscillatory laser flux during laser-driven combustion. The laser did not play a direct role in the pressure-driven response measurements. The primary objective behind these laser-driven experiments was verification of the hypothesis in the literature that suggests the laser and pressure-driven propellant responses are analogous to each other.

Advanced homogeneous propellants like HMX and heterogeneous AP composite propellants were tested under laser and pressure-driven experiments at pressures of 1, 2 and 3 atmosphere. Erikson at BYU has developed a model that predicts the behavior of HMX propellants under oscillatory combustion conditions and efforts also focused on comparisons between the experimental and numerical data.

One-dimensional energy balance analyses in addition to steady-state temperature measurements were used to evaluate the effects of condensed-phase heat release and gas-phase heat feedback on the propellant response amplitudes. Steady-state species measurements were used to validate gas-phase chemical mechanisms for HMX and the AP/HTPB propellants. These validated mechanisms were then used in a one-dimensional premixed flame code to obtain the steady and unsteady components of the gas-phase heat feedback.

An analytical model developed by Culick was used to perform parametric studies to evaluate the effects of gas-phase heat feedback and condensed-phase heat release on the
magnitude of the response functions. An analytical model based on the work of Iribicu and Williams, and Roh, Apte and Yang was also used to obtain the response function as a function of gas-phase heat feedback and condensed-phase heat release and was compared to the experimentally measured response functions.

Laser-driven response experiments on HMX showed that the response amplitude decreased with an increase in pressure. The unsteady component of the laser flux induces an unsteady component of the gas-phase heat feedback that is out of phase with the laser flux. The laser-driven experiments measured the response of the propellant to this net unsteady flux that is incident on the propellant surface. The increase in pressure increased the unsteady gas-phase heat feedback and hence decreased the net unsteady flux on the propellant surface and resulted in the lower response amplitudes. The pressure-driven response amplitudes increased with the increase in pressure because these experiments measured the propellant response to the unsteady gas-phase heat feedback that increased with pressure. Hence the laser and pressure-driven response experiments cannot be considered to be analogous for HMX. Comparisons with the numerical data of Erikson showed that the numerical model predicted a laser-driven response that is three times lower than the measured laser-driven response and predicts a pressure-driven response that is 50-70% lower than the measured pressure-driven response. Erikson believes this is due to poorly resolved condensed-phase kinetics and poor temperature sensitivity data. The analytical model of Culick also under-predicted the measured pressure-driven response profiles for HMX. Hence the analytical model of Iribicu and Williams was derived and provides reasonable agreement with the experimental values for pressure-driven response amplitude. This expression of Iribicu and Williams allowed for experimental inputs for the condensed-phase heat release and the gas-phase heat feedback. Clearly the difficulties in such experimental measurements reinforced the need for rigorous models that capture the appropriate physics. Comparison of the pressure and laser-driven response data with the theoretical transfer function of Son et al. showed that the transfer function severely under-predicted the experimental data at two and three atmospheres and slightly under-predicted the experimental data at one atmosphere. The
simplifying assumptions to the ZN approach result in only limited use to this transfer function and hence it is ill advised to use this transfer function to predict pressure-driven response based on laser-driven response data.

Laser and pressure-driven response amplitudes for the MURI 4 and 5 propellants decreased with an increase in pressure and laser flux due to the increase in the condensed-phase exothermicity and the decrease in the unsteady components of the net flux and gas-phase heat feedback incident on the propellant surface. The increase in pressure resulted in lower pressure-driven response amplitudes because the pressure change did not affect the gas-phase heat feedback but increased the exothermic heat release in the condensed-phase. The analytical model of Culick showed qualitative agreement in trends for the pressure-driven response function but continued to under-predict the experimentally measured values for the pressure-driven response function. The transfer function of Son et al. under-predicted the experimental data at both laser fluxes for the MURI 4 and 5 propellants. Clearly the limitations of the ZN approach results in limited use of this transfer function. The data clearly shows that the transfer function should not be used to obtain pressure-driven response data based on laser-driven experiments.

Laser-driven response amplitudes for the AP/energetic propellants showed no change with the increase in laser flux, while the pressure-driven response amplitudes decreased with the increase in laser flux. The changes in mean laser flux had different effects on the laser and pressure-driven response amplitudes and suggest different driving mechanisms. Hence the laser and pressure-driven response functions should not be considered as analogous experiments. Laser-driven response amplitudes for the HTPE propellants increased with the increase in laser flux, while the pressure-driven response amplitudes decreased with the increase in laser flux. Once again the different effects of laser flux on the laser and pressure-driven response functions suggests different driving mechanisms and hence disproves the hypothesis that the two experiments are analogous to each other.

Hence pressure-driven experiments coupled with detailed numerical models are essential towards obtaining predictive response functions for the advanced propellants.
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CHAPTER 1

INTRODUCTION, BACKGROUND AND OBJECTIVES

1.1 Introduction

The combustion process in a rocket motor is affected by the oscillations of the gas pressure in the combustion chamber. Response to these oscillations can trigger instability in combustion and lead to a potentially hazardous situation. Hence it is of prime importance to understand the dynamic response to these perturbations. Typically, oscillations in the motor are sustained by a power input of less than 0.01% of the energy released during combustion. Combustion oscillatory behavior is controlled by dynamic response of the combustion zone to flow disturbances and the damping processes in the combustor. Complete characterization of the combustion zone is necessary to understand and model oscillatory response of a propellant.

Over the years various theoretical and experimental techniques have been developed to study combustion instability. New experimental designs and methods, together with enhanced equipment capability have allowed for measurement of chemical species, dynamic burn rates and other parameters during combustion. Modeling efforts have also undergone vast improvements due to an improvement in computer performance and numerical methods. The current day modeling efforts require experimental data as input parameters or as a tool for validation. The prime objective of this study was to obtain experimental pressure and radiation driven thrust response data as a function of heat flux,
frequency and pressure. In the ensuing sections, a background of propellant combustion and the coupling between the propellant combustion and the unsteady pressure, heat flux and velocity will be given.

1.2 Background

1.2.1. Solid Propellant Combustion

Solid propellants in general consist of a mixture of chemicals cast into a matrix of binder to yield the mechanical properties needed to form a propellant grain. Most propellants contain both oxidizer and fuel in sufficient proportions to support combustion without any external sources. Solid propellants are categorized into homogeneous and heterogeneous propellants.

1.2.1.1. Homogeneous Propellants

Homogeneous propellants consist of fuel and oxidizer elements that are chemically bound together. Homogeneous propellants consisting of a single ingredient are called monopropellants. Many propellant oxidizers are monopropellants, e.g. HMX and RDX; however, monopropellants are not used as production rocket propellants. Typically they are combined with other ingredients to produce the desired mechanical, combustion and ballistic properties.

Double-based propellants consist of two ingredients, each of which is a monopropellant and can support combustion. These propellants are commonly made up of Nitrocellulose (NC) and Nitroglycerine (NG). Nitroglycerin is a plasticizer and is
added to the fibrous nitrocellulose to form a propellant. The mixture of NC and NG is so thorough that the resulting propellant can be considered to be homogeneous. A one-dimensional premixed flame zone characterizes homogeneous propellant combustion.

1.2.1.2. **Heterogeneous Propellants**

Heterogeneous propellants are often referred to as composite propellants and typically consist of solid oxidizer particles, such as ammonium perchlorate (AP), physically embedded into a fuel binder, such as hydroxyl terminated polybutadiene (HTPB). Aluminum or other metals are also added to the mix as high-energy fuels. Minor ingredients such as stabilizers, curing agents, catalysts and instability suppressants are also present [1]. Figure 1-1 shows the structure of a typical AP composite propellant. Figure 1-1 shows that these heterogeneous propellants may have multiple flames including both premixed and diffusion flames. The AP particles can self support combustion and hence have large monopropellant flames associated with them with diffusion flames along the edges of the monopropellant flame. In addition, there can exist a final diffusion flame that is formed due to reactions between the fuel rich fine oxidizer/binder species and the oxidizer rich monopropellant flame species.

To maximize performance in an AP composite propellant, it is generally favorable for the propellant matrix to contain as much oxidizer as possible (for ammonium perchlorate, a stoichiometric mixture is roughly 90% oxidizer). There is a theoretical packing density limit for the maximum amount of oxidizer that can be used with a single particle size. Using more than one particle size, in which the smaller sized particles fit in
the gaps between the larger particles, can allow the total oxidizer fraction to exceed this limit. Many propellants use a combination of small and large particle size distributions.

![Diagram of AP composite propellant](image)

**Figure 1-1** Structure of a typical AP composite propellant [2,3].

### 1.2.2. Solid Propellant Rocket Motors

A solid propellant rocket motor is a relatively simple device. It consists of a cylindrical case with propellant bonded to its inner surface, a hollow combustion chamber and a nozzle to direct the flow of gases out of the chamber. Figure 1-2 shows a schematic of a typical rocket motor. The propellant surface on reaching its melt
temperature, forms a liquid layer called the foam layer which contains a mass of bubbling
gaseous products and molten propellant. Final combustion gas and metal fuel products
are detected in the gas-phase flame region. These products are convected towards the
nozzle.

The thrust of the rocket motor can be defined by equation (1.1) [4].

\[ F_{thrust} = \dot{m}_{\text{burn}} A_{\text{burn}} c \]  
(1.1)

\[ c = u_{ex} + \frac{(P_{ex} - P_{amb})A_{ex}}{m} \]  
(1.2)

where \( c \) is the equivalent velocity out of the exit nozzle, \( A_{ex} \) is the nozzle exit area, \( P_{ex} \) is
the nozzle exit pressure and \( P_{amb} \) is the ambient pressure.
Specific Impulse, \( I_{sp} \), is given by equation (1.3). The numerator is the time integral of thrust, and the denominator is the product of the total mass consumed and the gravitational constant.

\[
I_{sp} = \int \frac{F_{\text{thrust}}}{g} dt = \frac{c}{g} 
\]

(1.3)

A well defined thrust versus time pattern is an important goal for a rocket motor. Equation 1.1 suggests that the thrust can be regulated in three ways: changes in the burning rate, burn area or specific impulse (via changes in \( c \)). Since the thrust is proportional to the burning area, an appropriate configuration of the propellant grain will allow a suitable thrust pattern. The propellant grain is cast by inserting a mandrel into the motor and casting the propellant around it. The thrust of the propellant changes with time since the burning area changes with time and an appropriately cast propellant grain will allow some control of the time-thrust pattern.

Thrust is also affected by specific impulse. Equations 1.2 and 1.3 show that the \( I_{sp} \) is related to the exit velocity. For an isentropic expansion, the exit velocity can be expressed in terms of the chamber stagnation temperature (\( T_{st} \)), stagnation pressure (\( P_{st} \)) and the fluid molecular weight (\( W \)).

\[
U_{ex} = \sqrt{\frac{2\gamma T_{st} R_s}{(\gamma - 1)W} \left[ 1 - \left( \frac{P_{ex}}{P_{st}} \right)^{\frac{\gamma - 1}{\gamma}} \right]} 
\]

(1.4)

For a given chamber pressure, the exit velocity (and hence specific impulse) is proportional to the chamber temperature and inversely proportional to the average molecular weight of the species. These quantities are dependent on the adiabatic flame
temperature and chemical species concentrations of the propellant. Hence the specific impulse is purely dependent on the thermodynamics and the chemical composition of the ingredients. The flame temperature and species concentrations of the propellant are functions of pressure but they are independent of the burning rates. Hence the specific impulse is independent of burning rate and is an intrinsic function of the propellant.

Thrust can also be changed by modifying the propellant burning rate. Conductive heat transfer from the gas phase to the propellant surface is one of the primary driving forces for the combustion processes, and hence the factors affecting the heat transfer also affect the burn rate. A high energy propellant tends to have a higher burning rate compared to a low energy propellant. This is due to the higher temperatures and steeper temperature gradients and hence, the higher heat transfer rates.

Some other influences on burning rate are particle size distribution of the fuel and the addition of catalysts. Catalysts tend to enhance the rates of reaction and hence the higher heat transfer and burning rates.

Combustion characteristics are also affected by additional influences like initial temperature, ambient pressure, external flowfields and heat sources. Higher temperatures and pressures result in higher burning rates due to the increase in the reaction rates and the heat transfer. Pressure affects the burning rate statically as well as dynamically. Changes in external conditions during propellant combustion affect the combustion characteristics of the propellant and it may result in two way interactions between the external conditions and the combustion processes. An increase in the chamber pressure could result in burning rate changes, which in turn can result in changes in the chamber pressure. It is possible for coupling to occur between several ambient variables like
Initial temperature, pressure, temperature fields, radiant heat fluxes, flow fields and the combustion characteristics like burning rate, flame temperature and gas velocity.

1.2.3 Unsteady Combustion in Rocket Motors

1.2.3.1 Acoustic Instability

The rocket chamber typically has acoustic waves that propagate at resonant frequencies. Frequencies associated with the acoustic waves vary from a few Hertz to several thousand Hertz. Figures 1-3, 1-4, and 1-5 show the acoustic modes for a typical rocket motor [4,5].

![Figure 1-3: Longitudinal Modes for a typical Rocket Motor [5].](image1)

![Figure 1-4: Tangential Mode [5](image2)](image2)

![Figure 1-5: Radial Mode [5](image3)](image3)

The lines within the chamber depict pressure waves. Most waves tend to dampen and die out, but if the resonant frequency of the rocket chamber coincides with the
resonant frequencies of the propellant, the waves may amplify and acoustic instability may result.

Instability results in large chamber pressure oscillations at the resonant frequencies. Instability could also result in a change in the mean pressure and is extremely undesirable in rocket motors. Acoustic waves are driven when fluctuations in acoustic velocity are amplified at an appropriate phase relative to the acoustic pressure. Acoustic velocity changes occur due to either mass addition or due to heat addition. Acoustic driving through heat/pressure interactions are described by the Rayleigh criterion. Rayleigh criterion is the cyclic integral of the pressure and heat fluctuations and is expressed by equation 1.5. A positive value indicates acoustic driving. Since combustion heat release is often pressure dependent and normally occurs at a higher rate with an increase in pressure, acoustic driving by combustion is a strong possibility.

\[
\int Q'P'dt > 0
\]  

(1.5)

Both means of acoustic driving may be present in a solid rocket motor. The burning rate may vary over the burn period. There is also tremendous heat release during combustion, and if a small amount of this heat varies in-phase with the pressure, acoustic driving may occur by means of the Rayleigh criterion.

The admittance function, \(A_b\), describes the propellant burning surface and its interaction with acoustic waves [6,7]. The admittance given by equation (1.6) is a complex number relating the fluctuations in velocity and pressure.

\[
A_b = \frac{u'/\bar{a}}{\left(\frac{p}{\gamma \cdot \bar{p}}\right)}
\]  

(1.6)
where $u'$ is the fluctuation in burned gas velocity, $a$ is the speed of sound, $\gamma$ is the ratio of specific heats. A positive $\text{Re}(A_b)$ suggests that the acoustic waves will be amplified.

**1.2.3.1.1 Acoustic damping**

Due to viscous damping, two-phase flow effects, and flow turning in the rocket motor, acoustic damping occurs and tends to dampen the unstable effects. Stability in rocket motors is divided into two domains:

a) Linearly stable motors
b) Linearly unstable motors

Small perturbations will decay and eventually damp out in linearly stable motors, while they will grow in linearly unstable motors. However, a large oscillation can occur in a linearly stable motor if the initial amplitude is large enough (greater than a threshold limit). The oscillations could now grow to a limit cycle that is determined by non-linear effects.

**1.2.3.2 Non-Acoustic ($L^*$) Instability**

Bulk mode instability [8] occurs at conditions where the combustion chamber volume to nozzle throat area ratio (a characteristic length, known as $L^*$) is small. The rocket chamber acts as a Helmholtz resonator and the pressure of the entire chamber rises and falls uniformly. Bulk mode instability is observed mainly during the early stages of burning and is observed only for a narrow band of frequencies. It is believed that bulk mode instability occurs when the burn rate leads the pressure in phase [5]. This is because the chamber acts like a one-way Helmholtz resonator because the throat is
choked and does not allow pressure fluctuations to propagate upstream. Hence the pressure rise can only be accomplished by increases in mass flow. Hence the bulk mode instability requires the burn rate fluctuations to lead the pressure fluctuations.

### 1.2.4 Response Functions

These response functions help isolate the coupling between the various ambient conditions (pressure, velocity) and the combustion characteristics (burning rate) described in previous sections. The use of such sub-models helps isolate the interactions between a given variable and the propellant burning rate. The propellant response functions listed here describe the effects of pressure, velocity and heat flux on the burning rate. This interaction of propellant combustion with the ambient can be quantified in terms of these response functions, which allow comparisons of different propellants.

#### 1.2.4.1 Pressure-Coupled Response

Acoustic and non-acoustic oscillatory combustion are thoroughly tied to the dynamic burn rate of the propellant. Propellant burning rate determines the rate of mass injection into the rocket chamber and hence directly affects the mean and fluctuating chamber pressures. The chamber pressure also has a strong effect on the burning rate. This influence of pressure on the burning rate is not instantaneous. This is due to thermal inertia. This dynamic influence of pressure on the burning rate is mathematically expressed as the pressure-coupled response, $R_p$, and is described by equation 1.7. The
pressure-coupled response is a complex function with an amplitude and phase component and is frequency dependent.

\[
R_p = \frac{\left( \frac{r'_b}{\bar{r}_b} \right)}{\left( \frac{p'}{\bar{p}} \right)}
\]  

(1.7)

where \( r'_b \) is the fluctuation in the burn rate, \( \bar{r}_b \) is the mean burn rate. \( p' \) is the fluctuation in pressure, and \( \bar{p} \) is the mean pressure.

The admittance can also be considered as a response function and is related to the pressure-coupled response function through equation 1.7 [6,7]

\[
A_n = \gamma \cdot \bar{m} \left( R_p - \frac{\left( \frac{\rho'}{\bar{\rho}} \right)}{\left( \frac{p'}{\bar{p}} \right)} \right) = \gamma \cdot \bar{m} \left( \frac{m'}{\bar{m}} - \frac{\rho'}{\bar{\rho}} \right)
\]  

(1.8)

If the pressure waves are assumed to be isentropic, then \( p \sim \rho' \gamma \) and equation 1.8 becomes equation 1.9 [6]. The ideal gas law can be used to express admittance in terms of fluctuations in pressure, temperature, and molecular weight fluctuations, such as in [1.10].

\[
A_b = \bar{m} (\gamma R_p - 1)
\]  

(1.9)

\[
A_b = \bar{m} \left( R_p - 1 + \frac{\rho'}{\bar{\rho}} - \frac{T'}{T} \right)
\]  

(1.10)
1.2.4.2 Velocity-Coupled Response

The velocity-coupled response compares the oscillation in burning rate to the cross-flow velocity and is given by equation 1.11. The hot gases that flow along the surface of a propellant in a rocket chamber accelerate towards the nozzle. This flow affects the boundary layer and enhances heat transfer from the gas phase to the propellant surface and hence increases the burn rate. This phenomenon is called erosive burning. There is also a fluctuating velocity component that occurs due to the longitudinal or tangential acoustic modes. These fluctuations may also lead to enhanced burning rates. The erosive burning can link itself to the acoustics in the chamber and result in acoustic growth. This is known as velocity coupling [9]. The acoustic velocity is 90° out of phase with the pressure, and so, for velocity coupling, it is the imaginary part of the response that couples the flow of energy from combustion processes to the acoustic field.

\[
R_u = \left( \frac{r_n'}{\bar{r}_n} \right) = \left( \frac{m'}{\bar{m}} \right) = \left( \frac{u'}{\bar{u}} \right)
\]  

(1.11)

where \( u' \) is the fluctuating velocity component and \( \bar{u} \) is the mean velocity.

1.2.4.3 Heat Flux Coupled Response

The pressure-coupled response is an important parameter in the analysis of combustion instability, but due to limitations and uncertainties in the measurements to determine it, heat flux coupled response measurements have become common in recent work. The heat feedback from the oscillating pressure during the pressure-coupled measurements is simulated through an oscillating external heat flux in the heat flux
coupled response measurements. The heat flux coupled response is mathematically expressed by equation 1.12. The response has an amplitude and phase and is frequency, mean heat flux and pressure dependent.

\[ R_q = \left( \frac{r_{b}^{'}}{r_b} \right) \left( \frac{q_{rad}^{'}}{q_{rad}} \right) \]  

(1.12)

1.3 Objectives

This study was part of a Multidisciplinary University Research Initiative (MURI) that was funded by the Ballistic Missile Defense Organization (BMDO). The primary objective of this initiative was to understand the connections between the chemical processes in the condensed and gas phases of a burning solid propellant, and unstable macroscopic fluid motions in the chamber of a rocket motor. Achieving this objective provided the basis for making small changes in the chemical composition of a propellant in order to produce decreased sensitivity of the propellant to unsteady motions. It also helped with modifications to the propellant combustion characteristics such as plateau burning behavior or the effect of size distributions of condensed material in the combustion products, thereby increasing the attenuation of unsteady motions by gas/particle fluid dynamic and combustion interactions. A key task of this program was measurement of pressure and velocity coupled response. The program was also responsible for transfer of these research results to the U.S. government and other research organizations with emphasis on understanding the propellants’ properties and
conditions required for design and operation of stable motors. Several different principal investigators located at different universities across the United States focused on objectives ranging from determination of chemical rate constants to the overall simulation of a rocket combustion chamber. As part of this study, three sets of AP composite propellants were obtained from commercial companies. The first set of propellants, listed as MURI 4 and 5 propellants, were AP/HTPB propellants and differed from each other only in curative type. The second set of propellants, listed as an AP/energetic binder propellant, contained an energetic binder instead of the relatively inert binder in the MURI 4 and 5 propellants. The third set of AP based composite propellants contained an energetic plasticizer and an energetic fuel. This class of propellants contained three propellants listed as AP/HTPE high rate, AP+AN/HTPE low rate and AP+AN/HTPE high rate. The only difference between the AP+AN high rate and low rate propellants was the average AP particle size.

As part of this overall initiative, the work presented in this thesis focused on laser and pressure-coupled response measurements for HMX as well as the three sets of AP composite propellants. HMX was studied as part of this program due to its homogeneity. HMX is considered to be an advanced energetic ingredient that could be used in some composite propellants. Since it is homogeneous, it has been modeled through one-dimensional steady-state models with well-established rate constants for gas-phase chemical reactions. Hence tremendous improvements have been achieved in the steady and unsteady modeling efforts for HMX over the last few years. Experimental study of this propellant helped perform comparisons with the unsteady modeling work being developed as part of this initiative. The objective was to validate these modeling efforts.
since comprehensive understanding of combustion instability can only be achieved through such numerical models. The experimental data was also useful in examining the validity of analytical response and transfer functions based on quasi-steady homogeneous assumptions. The three sets of AP composite propellants were also a vital part of this initiative. These propellants showed promise as the next generation of rocket propellants and were studied to evaluate the effects of unsteady phenomenon on their combustion characteristics. Due to restrictions on the formulations of these AP composite propellants, the effect of propellant formulations will not be discussed in detail.

The specific objectives of this study were:

1. Development of a test facility to measure pressure-coupled response at low pressure for a variety of propellants.

2. Develop an understanding of the effects of new ingredients and combustion modifying additives on the stability characteristics of propellants through pressure and laser-coupled response function measurements.

3. Obtain experimental data during laser and pressure-driven combustion experiments at different test conditions. Use the obtained experimental data to examine a relationship between laser and pressure-coupled response measurements.

4. Provide meaningful response data to other investigators to develop a mechanistic understanding of the unsteady combustion characteristics of new propellants.

5. Compare the experimental data to numerical, analytical and phenomenological models in an attempt to highlight the predictive capabilities of the models and suggest improvements based on experimental observations.
Chapter 2

LITERATURE REVIEW

Literature concerning experimental, modeling and theoretical studies pertaining to combustion instability is summarized in this chapter. The first section will cover the theoretical and modeling studies in combustion response functions, while the second section will focus on the experimental efforts. Most of the experimental combustion response studies used double-base propellants, instead of the heterogeneous MURI propellants or monopropellants such as neat HMX, but the experimental objectives in those studies are very similar to this study. Only the most relevant studies will be reviewed in this chapter.

2.1 Modeling Approach

2.1.1 Pressure-Coupled Modeling

Most work in combustion instability studies have followed two basic approaches: The Flame Modeling approach (FM) [6], and the Zeldovich-Novozhilov approach (ZN) [11]. The FM approach was used in combustion studies in the United States, while the ZN method was used in the former Soviet Union. The two methods are similar and follow the Quasi-Steady gas phase, Homogeneous propellant, and One-Dimensional (QSHOD) assumptions. Both approaches assume the condensed phase properties are constant, no distributed condensed-phase reactions take place, and propellant
gasification takes place only at the surface. The approaches assume a linear response and hence are valid only during small perturbations to pressure and burning rate.

Both approaches state that the unsteady burning rate is a function of the pressure and heat flux. The steady state burning rate is a function of the pressure and initial temperature. The ZN and FM approaches transform the steady state burning rate laws into corresponding unsteady laws. The ZN method can use experimental data as input, while the FM method uses mathematical models to supply the required parameters. However, it has been shown that both approaches reduce to the same form and are equivalent [12,13,14].

Equations (2.1) and (2.2) show the pressure-coupled response functions obtained under the FM and the ZN approach respectively.

\[
R_{p,FM} = \left( \frac{nAB + n_s (\lambda - 1)}{\lambda + \frac{A}{\lambda} - (1 + A) + AB} \right) \tag{2.1}
\]

where \( \lambda = \frac{1}{2} + \frac{1}{2} \sqrt{1 + 4i\Omega} \), \( \Omega = \frac{2\pi\alpha}{r_b^2} \) (dimensionless frequency) \( \tag{2.2 a,b} \)

\[
R_{p,ZN} = \left( \frac{\nu + \delta(\lambda - 1)}{\lambda r + \frac{k}{\lambda} - (r + k) + 1} \right) \tag{2.3}
\]

where \( k = \left( \frac{\partial \ln T_b}{\partial T_o} \right)_{p} \), \( \nu = \frac{1}{\left( \frac{\partial T}{\partial \ln p} \right)_{T_o}} \) \( \tag{2.4 a,b} \)
\[ r = \left( \frac{\partial F}{\partial T_s} \right)_p, \quad \nu = \left( \frac{\partial \ln \bar{\tau}}{\partial \ln p} \right)_T, \quad \text{and} \quad \delta = \nu r - \mu k \]  

(2.5 a,b,c)

The ZN parameters are derived from steady-state data while the FM variables are defined by burn rate laws and defined by equations (2.6), (2.7), (2.8), (2.9), and (2.10).

\[ r_b = A_s p^n \exp \left( -\frac{E_s}{RT_s} \right) \]  

(2.6)

\[ r_b = b p^n \] (b is a constant)  

(2.7)

\[ A = \left( T_s - T_o \right) \left( \frac{E_s}{RT_s^2} \right) \]  

(2.8)

\[ B = \frac{1}{\left( T_s - T_o \right) \cdot \sigma_p} \]  

(2.9)

\[ \sigma_p = \left( \frac{\partial \ln \bar{\tau}_b}{\partial T_o} \right)_p \]  

(2.10)

In the above equations \( A_s \) and \( b \) are constants, and \( E_s \) is the activation energy related to surface gasification. The ZN and FM equation are equivalent if \( A = k/r \), \( B = 1/k \), \( n = \nu \) and \( n_s = \delta/r \). These response functions are a function of frequency and have an amplitude and phase component. A detailed derivation of the response function based on the FM approach is presented in Appendix A.

The intrinsic instability of the propellant via the ZN or FM method is calculated by setting the denominator in equations (2.1) and (2.2) to zero. The stability requirements for the FM and ZN method are given by equations (2.11) and (2.12). The stability requirements are derived in Appendix B. Figure 2-1 shows a stability plot for the FM
and ZN approach. The figure plots the A or k/r parameter against k or 1/B. The values for some common propellants are also mapped out.

\[ A < \frac{B+1}{(B-1)^2}, \text{ (FM method)} \]  

(2.11)

\[ r < \frac{(k-1)^2}{k+1}, \text{ (ZN method)} \]  

(2.12)

Figure 2-1  A Stability Plot for some monopropellants [15].

2.1.1.1 Quasi-Steady Models

Modeling efforts in the 40’s and 50’s focused on a time delay between input parameters (pressure) and the output (burning rate). These time lag theories assumed there would be time lags for all processes, including condensed phase relaxation. However these models did not accurately predict experimental data [16,17]. Some theories did not predict a response peak while some others produced response peaks by
arbitrarily adjusting certain time lag parameters. This theory was therefore unacceptable.

Denison and Baum used QSHOD assumptions to derive a four parameter form of the response functions without any time lags [18]. This effort also used the flame sheet approximation and assumed that all reactions essentially occurred at the same temperature in a thin region. The KTSS model developed by Krier et al. used QSHOD assumptions to predict response functions [19]. Instead of using the flame sheet approximation where all energy is released in a single plane, this model used an approach where the energy release is spatially uniform over a gaseous layer of some thickness attached to the burning surface. The energy release over a finite gaseous thickness is representative of a process controlled by mass diffusion. The flame structure in an AP composite propellant is believed to be governed by diffusion and the KTSS model allows a composite flame structure to be examined. The model still uses simplified chemical kinetics with a single distributed reaction. Figure 2-2 shows a sketch of the KTSS model and the flame sheet approach.
2.1.1.2 Unsteady Gas-Phase Models

High frequency, high pressures and long propellant flame zones are some effects that cause the Quasi-Steady approach to fail [20,21,22]. Unsteady gas phase models are required to handle these conditions. T’ien developed a model with an unsteady gas phase [20]. This model used the flame sheet approach instead of the distributed energy...
release approach and included a single Arrhenius gas-phase reaction. T’ien observed that at high frequencies, the response did not approach zero, but showed a second peak that is associated with the gas-phase.

Williams and Margolis developed a model which was multi-dimensional and also included unsteady gas-phase effects [23]. The model used a simplified global reaction scheme and assumed constant density in the gas-phase region. This constant density assumption was believed to be valid for AP monopropellant combustion. The model was used to focus on intrinsic stability limits.

Huang and Micci used a one-dimensional, laminar, premixed flame approach with three gas-phase reaction steps [24]. The model assumed that the propellant decomposed according to the Arrhenius law with no condensed phase reactions. The ambient pressure is assumed to be uniform in space and only a function of time. This model and T’iens’ predicted similar peaking frequencies but varied in magnitude for the real part of the acoustic admittance.

Clavin and Lazimi developed a model with unsteady gas-phase effects. They combined two models to get the overall response function [21]. At low frequency, the QSHOD model was used, while at high frequencies the unsteady gas-phase effects were allowed to dominate and used as a limiting case. A simplified gas-phase reaction mechanism with a single step reaction was used in the model. The combined model allowed the response function to be plotted over a large frequency range.

Novozhilov developed a model which used time lags to treat unsteady gas-phase effects, while the condensed phase was treated by the ZN assumptions [25]. This model
assumed that the burning rate at a given time is a function of the instantaneous pressure and temperature at a previous time.

Erikson and Beckstead developed a numerical model for unsteady propellant combustion with detailed gas-phase chemistry and applied it to RDX and HMX [3,26]. The quasi-steady assumption was relaxed in favor of a fully unsteady gas phase. The model is the first attempt at using a detailed reaction mechanism for combustion under oscillatory pressure conditions. The quasi-steady and unsteady gas phase models are compared for RDX and HMX at pressure of 1, 8.5, and 68 atmospheres. The unsteady model predicts a second peak for all pressure at the higher frequencies. The quasi-steady and unsteady models predict similar values at frequencies ranging up to approximately 100 Hz.

Figure 2-3 (a) and (b) shows a comparison between the quasi-steady and fully unsteady modeling results for RDX at one and 68 atmospheres. The results show that the quasi-steady assumption appears to be valid below 100 to 200 Hz at one atmosphere and below 1000 Hz at 68 atmospheres. At 1 atmosphere, the deviation between the quasi-steady and unsteady values does not begin until after the peak, while at 68 atmospheres, the deviation is observed before the peak.
Figure 2-3 Quasi-Steady versus Unsteady Modeling Results for RDX [3].
2.1.1.3 Condensed Phase Reaction Models

In the condensed phase region, the characteristic reaction times are small relative to the thermal relaxation times and hence can be assumed to be quasi-steady. It was common to use an Arrhenius type relation to model the condensed phase reaction zone. High activation energy reactions will be limited to a narrow region where the temperature is relatively high. Hence the reaction can be assumed to be a surface reaction. However, the condensed phase reactions do become important under certain conditions and have been considered in the following efforts.

Culick was the first to include distributed condensed phase reaction in a quasi-steady combustion model [6]. The model used an inertial system of reference and assumed a uniformly distributed reaction in the condensed phase. The model also assumed that the properties were averaged over the chemical composition. The gas-phase was assumed to be quasi-steady with a Lewis number of 1. The model showed that the sub-surface decomposition acted as a damping agent. The heat release in the condensed phase was found to be inversely proportional to the maximum amplitude of the response function. The sub-surface decomposition decreased the maximum amplitude but did not change the frequency at which the maximum amplitude was detected. For exothermic decomposition, the real part of the response function is positive, while for an endothermic decomposition, it is negative. The response amplitude also showed a weak dependence on the sensitivity of the decomposition reactions to temperature. This work has been numerically modeled in this study and has been used to understand the effects of heat feedback and condensed-phase heat release.
on propellant response. This modeling effort will be discussed with the experimental data in chapters 5 and 6 of this thesis.

Price and Boggs developed a model for unsteady combustion which used two competing distributed condensed phase reactions, one exothermic and the other endothermic [27]. The gas phase is simplified, but uses an unsteady analysis based on a reaction progress variable. The model has been used to predict ignition transients, and deflagration to detonation transition but has not been used for pressure coupled phenomena. It appears that the model can be used in this area as well.

2.1.1.4 Non-Linear Models

Most models assumed that the deviations from the mean were small and hence allowed linear modeling. Large deviations from the mean result in products of perturbations that are large and result in non-linearities. The convective term in the energy equation is non-linear since the velocity is a function of temperature and vice-versa. This effect was accounted for in the following models.

Levine and Culick developed a model that used non-linear terms [28]. The gas-phase was considered to be quasi-steady, while the condensed phase decomposition was described by surface pyrolysis. The non-linear convective terms were retained in this analysis. The response was calculated for large pressure oscillations. Stability boundaries were calculated for a number of oscillation amplitudes and were noticed to be more restrictive than the models that used the linearized analysis.
Kooker et al. also studied non-linear behavior in a similar manner. They examined different numerical methods to solve their model [29,30]. Simulations on sudden increases in the pressure fields were performed. These simulations were characteristic of closed bombs and gun combustion chambers.

### 2.1.1.5 Applied QSHOD Models

QSHOD models allowed the unsteady theory to be applied to various steady-state models. This is particularly true for the ZN method. Steady state models have been used to provide the necessary parameters and the QSHOD theory is then used to obtain the response function. Beckstead developed a model where he obtained certain response parameters from the BDP (Beckstead, Derr, Price) steady-state model and applied it to unsteady theory [31,32]. The BDP combustion model for composite propellants was used to obtain A, B, and n parameters and FM theory then yielded the pressure response.

### 2.1.2 Heat Flux Coupled Modeling

There is a limited amount of data on modeling efforts for heat flux coupled combustion. Mihlfith et al. reported a new experimental technique in 1972 to measure combustion response to sinusoidal laser heating by measuring combustion recoil [33]. They also published a method to convert the recoil data to a dimensionless burn rate response. This led to efforts towards heat flux modeling.

Iribiciu and Williams studied the effects of heat flux on propellant combustion [34]. They believed in the presence of a critical zone in which the chemical kinetics controlled
the burning rate and showed that the radiation must be absorbed either into this zone or just below it for the radiation to augment the burning rate. They also discussed the equivalence principal that suggests the absorbed radiant heat flux has an effect similar to a rise in initial propellant temperature.

DeLuca published analytical expressions for a heat flux coupled response function, $R_q$, as well as a pressure coupled response function, $R_p$, using the FM approach [35,36,37]. Son et al. used an approach similar to the ZN method, to obtain an expression for $R_q$ [38]. They also developed a ZN form of $R_p$ with an incident radiant heat flux [39,40,41]. The ZN forms of $R_p$ and $R_q$ are given by equations 2.13, and 2.14.

Son et al. and DeLuca developed a relationship (transfer function) between $R_p$ and $R_q$.

$$R_p = \frac{\nu + \delta (\lambda - 1)}{\lambda r + k - (r + k) + 1 - \frac{Q_r k (\lambda - 1)}{\lambda (\beta + \lambda - 1)}}$$

(2.13)

$$R_q = \frac{\nu_q + \delta_q (\lambda - 1)}{\lambda r + k - (r + k) + 1 - \frac{Q_r k (\lambda - 1)}{\lambda (\beta + \lambda - 1)}}$$

(2.14)

where

$Q_r = f_r J$, $f_r$ is the fraction of radiant energy absorbed below the surface.

$$J = \frac{q_{rad} \rho_b}{C_{p,c} (T_x - T_o)}$$

$\beta = \alpha_r K_{abs}/r_b$, $K_{abs}$ is the Beer’s law absorption coefficient,

$\delta_q = \nu_q r - \mu_q r$, $\nu_q$ and $\mu_q$ are given in equation 2-15 and 2-16, and $k$, $r$, $\nu$, $\mu$ and $\delta$ are ZN parameters.
\[
V_q = \left( \frac{1}{\partial q_{rad}^{\ln} r_0} \right)_{T_{e,p}},
\]

\[
\mu_q = \frac{1}{(T_s - T_e)} \left( \frac{\partial T_s}{\partial \ln q_{rad}} \right)_{T_{e,p}}
\]

### 2.1.3 Other Propellant Models

Several research groups have focused on modeling the steady state combustion behavior of propellants like RDX and HMX \ [43,44,45]\. Models have been developed for homogeneous propellants with more than one ingredient such as RDX/GAP pseudo propellant \ [46]\. The unsteady ignition process of monopropellants like RDX has also been studied \ [44]\. 

The following models pertain to analysis of propellant combustion and its interaction with flow within rocket motors. These models were restricted to homogeneous double-based propellants due to the vast amounts of experimental data available although the modeling group is developing efforts to study the effects of acoustic oscillations on AP composite propellants.

Roh developed a two-dimensional model that studied the effect of acoustic oscillations on homogeneous propellants \ [47]\. The objective of the model was to study heat release processes and their interactions with flow oscillations in rocket motors. The model used reduced kinetic mechanisms for gas and condensed-phase reactions. Two global reactions were used in the condensed phase and five reactions were used in the gas-phase. The model assumed that the thermo-chemical properties were constant in the
condensed phase region. The steady-state solution is used as a known condition and a periodic pressure oscillation is imposed at the chamber exit. The amplitude of pressure oscillation is 2% of the mean pressure. The model shows that there is a very large increase in the axial velocity fluctuation in the near field region while the increase in the vertical velocity fluctuation takes place in the secondary flame region. This large increase in the vertical velocity fluctuation was a result of the density change across the flame. The temperature fluctuation plots showed that the large fluctuation occurred in the luminous flame region where the NO species underwent reduction reactions. The temperature fluctuation plots showed strong coupling between the flame and the acoustic waves. The flame moved periodically in the vertical direction with the local pressure oscillations. The authors used the Rayleigh criterion (integral of the product of fluctuating pressure and heat release) to investigate the stability characteristics and found that the luminous flame zone played a large role in the stability of the motor due to large fluctuations in temperature and heat release. The net value of the product of pressure and heat release was positive and suggests that the acoustic wave would be amplified.

Roh enhanced his previous study to include coupling between the gas-phase and condensed phase processed during acoustic oscillations in a rocket motor [48]. In this study, the propellant burning rate was not set to its steady state value. The instantaneous burning rate was treated as part of the solution and interaction between the near-surface and condensed-phase processes was the focus of interest. The study used the reduced chemical mechanisms and assumed constant properties in the condensed phase. A quasi-steady assumption was used to determine sub-surface pyrolysis. An asymptotic
expansion was used to describe the propellant burning rate as a function of the local heat fluxes. Once again the amplitude of pressure oscillation was 2% of the mean pressure. The axial velocity fluctuation in the near-surface region is much less than in the case where the steady state burning rate was used. The vertical velocity fluctuation appears to be identical to the previous study. The temperature fluctuation was once again observed in the luminous flame region where the NO reduction reactions took place. The amplitude of the temperature fluctuation was similar to the previous study but the phase was quite different. The difference is primarily due to the transient response of the condensed phase. The large variation in phase caused qualitative changes in the heat-release characteristics. The burning rate of the propellant lagged the pressure fluctuation by about 20° across the propellant surface. The Rayleigh criterion was used to study the stability characteristics and showed that the transient condensed phase may have changed the time evolution of the local heat release. The distribution of Rayleigh’s parameter showed the presence of a positive and a negative peak of equal amplitude. The net value of the product of unsteady pressure and heat release was positive and suggested that the acoustic fluctuations within the chamber would be amplified.

2.2 Experimental Studies

Several expressions for pressure-driven or radiation-driven combustion response functions have been theoretically derived under the FM and ZN frameworks and have been presented earlier. Many experimental studies have been conducted to verify these combustion response functions. Most of the work was conducted for measurements of
pressure-driven combustion response. Price [5] and Strand and Brown [49] have reviewed the test apparatus for pressure-driven combustion response. Strand and Brown gave a detailed comparison of the different test methods used to measure the pressure-driven combustion response. Since several disadvantages existed for each method, new techniques have been developed continuously. Due to the relative difficulty in obtaining pressure-coupled response data, heat flux driven experiments were performed by a number of researchers. The heat flux driven experiments are believed to be analogous to the pressure-driven experiments and hence have been the focus of many research groups for the past few years.

2.2.1 Heat Flux Response Experiments

Mihlfeith et al. [33] were the pioneers in the experimental study of the heat flux response function. In 1972, they obtained combustion response to sinusoidal laser heating by measuring combustion recoil. They also used perturbation theory to help obtain a simplified expression for the dimensionless burning rate in terms of experimental parameters that were easy to measure. Since then experimental studies of combustion response to external radiation have been carried out by several other research groups. The laser-driven combustion response over a wide range of frequency has been experimentally obtained by the method. Most of the laser-driven response data was for burning rate response. In addition to burning rate measurements, Parr et al. [51] and Finlinson et al. [52] have recorded images of the CN flame through PLIF and an intensified CCD camera.
Mihlfeith et al. used a 5.0 kW xenon-mercury arc lamp combined with a chopper to generate a periodic heat flux and a sensitive quartz force transducer to measure the transient force. All tests were conducted at atmospheric pressure. Figure 2-4 shows a schematic of the experimental setup. The combustion responses for UAX (80% AP, 18% Polyurethane, B. F. Goodrich Estane based, and 2% N-butyl ferrocene catalyst) and UCX (80% AP, 17% Polyurethane, B. F. Goodrich Estane based, 2% N-butyl ferrocene catalyst, and 1% Carbon black) were investigated.

Figure 2-4 Schematic of Laser Recoil Setup [33].

Maximum response occurred at dimensionless frequencies $\Omega$, ($\Omega=\alpha\omega r^2$), of 20 to 80. The location of the maximum response value depended on the fuel binder, oxidizer loading, and propellant translucence. It was observed that the combustion response was
affected by a change in the propellant composition. A theoretical calculation was also performed in their study. For the UCX propellant, quantitative agreement between calculation and experiment could be obtained by choosing appropriate values of required theoretical parameters. For the UAX propellant, the magnitude of the maximum response was accurately predicted, but the frequency for the measured maximum response was lower than the predicted frequency. Keeping the key theoretical parameters constant resulted in approximate predictions of the measured results.

Strand et al. used microwave doppler velocimetry to measure the combustion response to an oscillating thermal radiation source (CO$_2$ laser) [53]. The laser was modulated sinusoidally at heat flux magnitudes from 0 to 100% of full power over the frequency range of interest. Tests were carried out at a mean pressure of 2.1 MPa (300 psia) and frequencies from 50 to 900 Hz using A-13 (76% AP, 20.4% PBAN-787, 3.6% Epon Resin-828) and modified A-13 propellants (containing a slight amount of carbon). The results showed that transmissivity was not a significant factor at the CO$_2$ laser wavelength, 10.6 $\mu$m. The results for A-13 propellants agreed with existing results of the pressure response function in magnitude and frequency. A transfer function relating the pressure response function ($R_p$) to heat flux response function ($R_q$) was derived in their study. Given certain assumptions, the transfer function was simplified to $R_p / R_q = n$. $n$ denotes the exponent term for the burning rate equation (Saint-Roberts equation). The calculated results for the heat flux response function were compared to the experimental data. The response magnitude for the predicted peak was 40% greater than
the experimental value, and the frequency for the predicted peak was lower than the experimental value.

Simonenko et al. studied fluctuations in burning rate with and without an external periodic heat flux [54]. The instantaneous burning rate was determined by measuring the instantaneous reactive force of the combustion products from the surface. A relationship between the reactive force and burning rate was obtained by performing steady state calibrations. Sinusoidal heat flux was obtained from a powerful xenon lamp. The natural frequencies of the burning rate fluctuations were measured at pressures from 1 to 40 atmospheres and initial temperatures ranging from 20 to 120°C. The experiments were conducted using samples including H (56.5% weight nitrocellulose, 28% weight nitroglycerine, 11% weight dinitrotoluene, 4.5% weight additives), H+1% carbon black (H+CB), H+1% PbO (N+Cat), and H+1%Pbo+1%C (H+CB+Cat). They used self-sustained combustion experiments to determine the characteristic (natural) frequency of the propellant. During heat-flux imposed experiments on the propellants, the amplitude of the burn rate response was observed to increase from a low value at low frequency to a maximum and then decrease with an increase in frequency. The maximum amplitude was observed to lie at the characteristic frequency detected under the self-sustained combustion experiments. This resonant frequency was also observed to increase with burning rate. The trend agreed with the following relationship determined by the ZN approach.

\[
f_0 = \sqrt{k/(2 \cdot \pi \cdot r)} \cdot \frac{u^2}{\alpha}
\]  

(2-17)
where $u$ is burning rate, $\alpha$ is the thermal diffusivity, $k = \beta(T_s - T_0)$, $T_s$ is the surface temperature, $T_0$ is the initial temperature, and $r = \partial T_s / \partial T_0$.

The calculated values for the natural frequency were three to six times lower than the experimental values. The calculated natural frequency used experimentally determined values for the surface temperature and $r$. Experimental errors in the measurement of these parameters compounded with theoretical deficiencies in the expression for the natural frequency could account for the large disparity between theory and experiment.

Zarko and his co-workers also studied unsteady burning subjected to oscillatory radiation [55]. A xenon 10-kW intensity lamp was used as radiation source in most tests, although a 40 W CO$_2$ laser and a 70 W YAG-Nd+3 were used in some tests. The samples (including H, H+1% C, and H+1% PbO) were cylindrical, 4-6 mm in length and 5-16 mm in diameter. Tests included steady state laser-assisted combustion and combustion response to step or periodic heat flux. The steady state data was used to examine whether or not the radiation heating was only a preheating effect on the solid phase. The results showed that partial absorption of the radiation could result in an increase in the chemical reaction rates in the condensed-phase. It is important to mention that this conclusion was based on experimental observations during the combustion of double-based propellants and not on any strong physical/theoretical postulates.

In the step heat flux tests, the samples were subjected to a step decrease in heat flux. Several trends were observed. Firstly, combustion was extinguished with a step
decrease of 3 cal/cm² sec in an inert environment, but combustion continued with the same decrease of heat flux in air. Secondly, more transparent double-base propellants required a steeper decrease in radiation for extinction to occur. Thirdly, an increase in the ratio of \( \frac{q}{c \rho u_0 (T_{s0} - T_0)} \) decreased the combustion recoil for the double-base propellants, where \( q \) denotes the absorbed radiation flux.

In the periodic heat flux experiments, tests were conducted using double-base propellants at a 20-120°C initial temperature and 1-50 atmosphere pressure range. To facilitate the use of a linear analysis, the samples were subjected to small variations in the amplitude of heat flux. The results were in agreement with theoretical predictions. As \( u_0 \) increased, the resonant frequency increased monotonically. For the same \( u_0 \), the resonant frequency decreased with an increase in initial temperature. Phase information for the burning rate response could also be determined in their study. Zarko et al. recommended that it was better to determine \( r \) from the resonant frequency (equation 2.17) and \( k \) than from directly measuring the surface temperatures at variable initial temperatures during steady state condition.

Brewster and his co-workers wrote a series of papers on unsteady combustion subjected to external radiative heating [38-42, 56]. In reference 40, they developed a theoretical burning rate model to relate the heat flux response to the pressure response. Thus, the pressure response could be predicted through the heat flux response and the transfer function that related the two. In their work, the combustion phenomenon was assumed to be one-dimensional, quasi-steady in the gas-phase, with a homogeneous condensed phase. High activation energy in the gas-phase was assumed, which is
equivalent to a flame sheet approximation. In-depth absorption with no sub-surface chemical heat release was also assumed. To validate the flame model, the modeling results were compared to experimental data for A-13 composite propellant. With variation of the value of activation energy, the model could predict the pressure response or heat flux response, but could not predict both simultaneously. This suggests that the model needs refinement in its transfer function.

Son and Brewster showed a new approach to obtain the laser-driven response function over a wide range of frequencies from a single test using a series of radiant pulses, instead of a sinusoidal heat flux [39]. The experimental results for an AP/HTPB propellant were obtained using the new approach. The results showed that an increase in mean heat flux decreased the oscillating level of the response signal. The resonant frequency occurred at 200 Hz, and a phase lag was observed over the entire range of frequencies. This phase lag was very different from the experimental results and theoretical response function for double-based propellants [50,53,56]. Unfortunately, these differences were not explained in their study.

In reference 40, a linear expression for the radiative heat flux response as a function of primary experimental parameters was obtained. The expression was developed under the framework of the ZN approach and was similar to the expression derived from the FM approach. The linear effects of mean heat flux level and in-depth absorption on $R_q$ were addressed in their study. Due to these effects, the relationship between $R_p$ and $R_q$ was more than just a constant scaling factor. However, the ratio of $R_p$ to $R_q$ could be simplified to the constant scaling factor, if $R_p$ and $R_q$ were obtained at the same pressure
using a small mean heat flux and energetic material with a large absorption coefficient. They also suggested that the heat flux response could be measured by a series of heat flux pulses, instead of a sinusoidal wave. The method was useful when only a pulsed radiative source was available. The approach could also significantly decrease the testing time required to properly characterize a propellant.

Parr et al. [51] imaged the CN radical location in HMX flame at a heat flux of \(38.5 \pm 28.5\) W/cm\(^2\) using PLIF and flame chemi-luminescence. The frequencies of the heat flux ranged from 2 Hz to 5000 Hz. The amplitude and phase results showed that the resonant peak occurred at approximately 20 Hz. Oscillatory burning models with unsteady gas-phase analysis predicted a second peak at high frequency [20,24]. However this increase in thrust response amplitude at higher frequency was not observed and they concluded that the quasi-steady state assumption for the gas-phase was reasonable during oscillating burning of HMX.

Finlinson et al. theoretically and experimentally investigated laser-driven combustion response at atmospheric pressure [52]. Three theoretical burning models were developed to predict the pressure-driven response from the data of the laser-driven combustion response. Experiments were performed using a CO\(_2\) laser as a heating source. The laser was also used as a source for the oscillatory heat flux. A micro-force transducer was used to measure thrust. The burning rate was derived from the thrust time trace. N5 (double base), A13 (PBAN, AP), and NWR11 (HTPB, AP, minimum smoke) were used in their study. The samples were tested at mean heat fluxes ranging from 4 to 49 cal/s/cm\(^2\). Based on the instantaneous burning rate, the magnitude and
phase as a function of non-dimensional frequency, $\Omega$, were obtained. The experimental data agreed with the theoretical results.

Finlinson et al. subsequently measured nitramine propellants, HMX and RDX, using the same technique [50]. In addition to burning rate response, flame height and light emission responses were also obtained in their study. An intensified CCD camera and photodiode measured flame height and light emission, respectively. Experiments were conducted at a heat flux of $35 \pm 27$ W/cm$^2$ over a frequency range from 2.5 to 1000 Hz. The average burning rates were 0.08 and 0.054 cm/s for HMX and RDX, respectively. The oscillation amplitudes for HMX thrust and light emission were approximately double those for RDX thrust and light emission. The HMX thrust response indicates that the resonant peak occurred between 20 to 30 Hz, while light emission response shows that the resonant frequency was around 10 Hz. The resonant peak for RDX thrust response was not well defined. The researchers concluded that the oscillatory burning was reasonably quasi-steady because the phase difference between the thrust and flame height was less than 30°.

Finlinson [57] extended his previous work and measured the laser-driven combustion responses for the N5 (catalyzed double-based propellant) at pressures ranging from 1 to 9 atmospheres. Three different levels of laser oscillation were used and it was found that the amplitude of thrust oscillation increased with an increase in the amplitude of laser oscillation. Finlinson also found that the relative phase changed from a lead at low frequency, to lag at higher frequency. The cross over point decreased from 32 Hz at an oscillatory level of 9 W/cm$^2$, to 18 Hz at a laser oscillation amplitude of 25
With an increase in pressure, the thrust response decreased in amplitude and the maximum shifted to a lower dimensional frequency. The theoretical studies suggest that the frequency at which the maximum response amplitude is detected increases with an increase in burning rate. The response amplitude is believed to be a function of the condensed-phase thermal relaxation time. The condensed-phase thermal relaxation time decreases with an increase in burning rate and hence should shift the maximum response amplitude to a higher dimensional frequency. Thus, the experimental observations of Finlinson are not consistent with theoretical studies.

2.2.2 Pressure-Driven Response Experiments

A number of devices including T-Burners, impedance tubes, ultrasound transducers, rotating valves, microwave systems, L* burners, and MHD flow meters have been used in the past to measure pressure response. At high frequencies, slot-vented T-Burners, magnetic flow meters and a modulated throat-damping burner are primary devices.

Figure 2-5 shows a schematic of the T-Burner. The propellant samples are loaded into the end caps, which are attached to the device. The burner is connected to a surge tank that is pre-pressurized with nitrogen to the desired mean pressure. When the propellant is ignited, the reaction products flush the cold nitrogen from the burner and oscillations develop and grow exponentially as observed in figure 2-6. The hollow cylinder of the burner acts as a pipe for longitudinal acoustic oscillations with pressure anti-nodes at each end. The samples are located at the pressure anti-nodes to ensure
optimum acoustic driving. Pressure time traces as shown in figure 2-6 are obtained using one or more transducers.

Figure 2-5 Schematic of a T-Burner (Center Vented) [5]

Figure 2-6 Pressure-Time trace from a T-Burner. [5]
The pressure time trace can be described by

\[ P' = \hat{P} e^{i\omega t} e^{\alpha t} \]  \hspace{1cm} (2.18)

where for \( \alpha > 0 \), the oscillations increase with time, and \( \alpha < 0 \), the oscillation decays with time.

When the propellant burns out, the oscillations decay in a roughly exponential manner. Appropriate values of ‘\( \alpha \)’ parameters; characterize both the growth and damping regions. The ‘combustion alpha’, \( \alpha_{\text{comb}} \) can be obtained by combining the two. The alpha combustion is an indicator of the amount of driving due to combustion. The pressure-coupled response can be obtained from the \( \alpha \) parameters using equation 2.20.

\[
\left( R_p \right)_{\text{real}} = \left( \frac{\frac{\gamma}{\bar{M}_b} a_o s_c \alpha_g - \alpha_d}{\frac{\gamma}{\bar{M}_b} a_o s_b \alpha_g - \alpha_d} \right) \] \hspace{1cm} (2.19)

\[
\left( R_p \right)_{\text{real}} = \frac{1}{\gamma \cdot \bar{M}_b a_o s_c a_b s_b} \frac{\alpha_g - \alpha_d}{4f} \] \hspace{1cm} (2.20)

In equation 2.20, \( \gamma \) is the specific heat, \( \bar{M}_b \) is the mean mach number at the combustion zone, \( a_o \) and \( a_b \) are the speed of sound in the overall chamber and the combustion zone respectively, \( s_c \) and \( s_b \) are burner cross-section and burning surface areas, and \( f \) is the oscillation frequency.

Finlinson et al. have measured the pressure-coupled response for RDX and HMX using the T-burner [58,59]. The samples were pressed in a die to 1.5 inches in diameter with a hole of 0.45 inches. Center pulsing through the experimental samples was used as
it provided the best results. Pulses during-burning and after the burn were used to obtain the decay rate during burn and after burn.

At pressures below 100 psi RDX and HMX were observed to have thick melt layers that tend to run off the vertically oriented sample in the T-burner and caused large errors. Hence experiments were restricted to pressure ranges of 200-1000 psi [1.35-6.8 MPa]. A large amount of scatter was observed in the results. The results for RDX and HMX showed that an increase in pressure resulted in a larger magnitude of the response function. The pressure increase also shifted the peak to a higher dimensional frequency. At 200 psi, the maximum response amplitudes were 0.7 and 1.2 for RDX and HMX respectively. At 1000 psi, the maximum response amplitudes were 2 and 2.5 for RDX and HMX respectively.

In reference 59 Finlinson compares his T-burner data for HMX to modeling analysis performed by Beckstead et al. in 1996 [13]. In that citation, Beckstead noted that an increase in pressure resulted in a decrease in the maximum response amplitude for HMX. The HMX data obtained by Finlinson showed considerable scatter and appears to show no distinct change in maximum amplitude with an increase in pressure. The increase in pressure does increase the location of the peak in response amplitude from 400 Hz at 200 psi, to 2000 Hz at 500 and 1000 psi. Comparison of the T-burner data with the WSB model showed poor agreement [42]. Subsequent modeling efforts by Erikson and Beckstead [3] have shown that an increase in pressure does indeed increase the maximum response amplitude of HMX and hence would appear to agree with Finlinson’s conclusions in reference 58.
Finlinson et al. have also obtained pressure-response data for ultra fine AP particles [60]. They compared the pressure-coupled response data for ultra fine AP particles (UAP) against the nitramines like HMX and RDX. The frequencies examined ranged from 130 to 2500 Hz. The response for UAP at 500 psi [3.4 MPa] shows the non-dimensional response decreasing from 4 to 1 as the frequency increases from 130 to 900 Hz. The 1000 psi. data shows the response increase from zero at 130 Hz to 4 at 2000 Hz. The 1800 psi. data showed a large amount of scatter and could not be interpreted in terms of a trend. The scatter in the data did not allow any interpretation of the effect of pressure on the maximum response amplitude. The maximum amplitudes were observed to lie around an $\Omega$ of 20 to 30. Comparison of the data with modeling showed good agreement at 500 psi but poor agreement at 1000 psi.

Brown et al. used a rotating valve method to measure the combustion response function [61]. This method used a small rocket motor with a conventional nozzle to control the combustion pressure. A secondary orifice was periodically opened and closed through a specially designed rotating valve to generate small amplitude pressure oscillations in the rocket motor. The frequency of the oscillations was controlled through the rotational speed of the valve. Thus small amplitude of pressure oscillations were generated in the rocket motor at selected pressures and frequencies. Figure 2-7 shows a schematic of the rotating valve. Various transducers were used to measure the steady state and oscillating component of pressure. The geometry of the rotating valve was modified to prevent any phase errors due to harmonic waves.
The modulations are generated in the low-frequency bulk mode and are much lower than the lowest acoustic mode of the burner. This allows the spatial variation in pressure to be neglected. The amplitude and phase of the pressure oscillations relative to the area oscillations are measured and the response function is then derived using these parameters in a transient ballistic analysis. The frequencies tested ranged from 300 to 800 Hz.

Comparison of this technique with the T-burner showed favorable agreement for propellant UTP-3001 at 340 psia. Comparisons with T-burner data for propellants A-13 at 130-200 psia and ANB 3066 at 490-530 psia also showed reasonable agreement. There was disagreement in the data for UTX-8501 at 200 psi. The characteristic exhaust

Figure 2-7 Schematic of the rotating valve method [61].
velocity for UTX-8501 was only 50% of the theoretical value while the characteristic velocities of the other propellants were about 95% of theoretical value. Hence the disagreement between the rotating valve and T-burner data for UTX-8501 was believed to be due to variable propellant composition and physical properties. The technique also showed that the response function was particularly sensitive to the errors in phase-angle measurement. The substantial reduction in the number of tests required to characterize a propellant compared to the T-burner made this technique a viable option.

Strand et al. used a microwave doppler phase shift technique to obtain a solid propellant pressure-coupled response function [62]. This technique allowed direct measurement of the transient regression rate of the solid propellants. The previous techniques required mathematical analyses to obtain a response function. The regression rate was measured by shift in phase angle between the incident and reflected signals. The phase angle shifts with the reduction in length of the burning strand and hence a rate of change of phase angle is proportional to the regression rate. Figure 2-8 shows a typical assembly and schematic of the technique. Since the technique is based on observing the movement of the condensed/gas-phase interface, roughness of the propellant surface, compressibility and system vibration could result in erroneous measurements. If the surface roughness is small compared to the microwave wavelength in the propellant, the microwave signal is thought to be reflected from a plane that is defined by the rms of the roughness. It was also verified that for the typical roughness scale of burning propellants, the propellant surface appears to be planar to the microwave signal. Response data was collected on various propellants at frequencies
ranging from 100 to 1000 Hz. Modifications could allow the high frequency limit to be increased to 1800 Hz.

Comparisons of the measured pressure-coupled response with data from T-burner and rotating valve for propellant A-13 showed good agreement. All the techniques seem to detect a multimodal response function curve. Comparisons with the rotating valve for propellant ANB-3066 showed poor agreement. The microwave burner detected a maximum response of 4 at 500 Hz, while the rotating valve detected a response value of 2.

Figure 2-8 Schematic of the Microwave Burning Measurement Technique [62].
Comparison of the microwave burner data for ANB-3066 with T-burner data also showed a large disparity. The T-burner showed the maximum response at 1000 Hz, while the microwave burner showed the maximum response to occur at 500 Hz. The larger microwave values compared to the T-burner and the rotating valve are believed to be due to the irregular burning rate and surface roughness effects of the propellant.

The microwave burner tests require significantly less turn around time compared to the rotating valve and the T-burner. Analysis of the response functions showed that the data obtained by this technique was not consistent [62]. This lack of consistency is due to the fact that the technique does not measure surface roughness and instead measures the root mean square surface.

Micci et al. used a magnetic flowmeter device to measure the velocity oscillations of the gases coming off a burning propellant surface within an excited combustion chamber [64,65]. Figures 2-9 and 2-10 show schematics of the technique.
This method is capable of measuring response into the high frequency modes (2000-10000 Hz). Unlike the T-burner which relies on indirect acoustic analysis to determine propellant response, this technique measures two or more acoustic quantities and allows for direct measurement of the propellant response. This technique uses Faraday’s law to generate an electrical field that is proportional to the flow velocity of the conductor (propellant gases), and the magnetic field. The combustion chamber is placed within the field of a permanent magnet. Two thoriated tungsten electrodes within the burner detect the electrical potential produced as the propellant burns past the two probes. These electrodes are placed several millimeters into the flow and the measured potential is proportional to the magnetic field strength, the distance between the
electrodes and the instantaneous flow velocity. A toothed gear is placed near the sonic
goatle and is driven by a variable speed motor. The pressure within the chamber is
modulated by chopping the exhaust through the nozzle with the gear. The instantaneous
pressure within the chamber and the position of the burning surface are measured by
transducers. These quantities are used to determine the acoustic admittance and hence
the response function for the propellant.

Figure 2-11 shows a comparison between the T-burner and magnetic flowmeter
burner pressure-coupled response data for a typical AP/HTPB Propellant. Comparison
of response data between the flowmeter burner and the T-burner assembly shows good
agreement in the amplitudes below 400 Hz and at 1800 Hz, and reasonable agreement in
the intermediate regime [49].

Cardiff et al. have used the magnetic flowmeter burner to measure response
functions for various heterogeneous propellants including aluminized AP composite
propellants [66,67]. Aluminized propellants were adhering to the nozzle and the toothed
gear at the exit. In order to prevent erosion, a high-pressure nitrogen flow was used to
cool the gear. A graphite nozzle insert was added to the setup to further reduce erosion.
Figure 2-10 Detailed Schematic of Combustion Chamber used in the Magnetic Flowmeter Burner [66]
Various formulations of AP/HTPB propellants were tested and compared to T-burner data obtained from Blomshield at NAWC. The data for propellant 1a was obtained at a pressure range of 410-550 psi (2.9 MPa – 3.9 MPa). The T-burner data was obtained at 300 (2.04 MPa) and 1000 psi (6.8 MPa). The flowmeter data lies in between the T-burner data. The maximum response is reached at 700 Hz, which corresponds to a non-dimensional frequency of 14. The real part of the response function increased from 0.5 to 2.5 at a non-dimensional frequency of 14 and then decreased to 1.5 at 40. The response values for propellant 4 and 5 will be presented in later sections to facilitate comparisons with the data obtained for those propellants in this study.

Finlinson et al. used magneto-hydrodynamic instrumentation on a T-burner to obtain simultaneous measurements of pressure-coupled response and velocity field
oscillation measurements [68]. The specific objective of their work was to determine the flow field away from the propellant surface. Pulse firings were used to initiate unstable behavior in the propellant samples and the ignition and burnout were recorded on photodetectors. A permanent yoke magnet and gauss-meter probes were used to create and detect the strength of the magnetic field. The technique was used on AP, HMX, RDX and AP/HTPB propellants at pressures of 200, 300 and 1000 psia (1.36, 2.04 and 6.80 MPa). Due to the presence of the melt layer in RDX and HMX, the pulses were disruptive to the combustion process. The relative phase and amplitude of the MHD oscillations were compared to the AC pressure signal through a cross-correlation program. The oscillation levels were observed to be highest near the propellant surface for test AP3. This was counter-intuitive because the velocity oscillations are higher away from the surface. The authors believe that the higher signal levels near the propellant surface are due to gas phase ion concentration levels that are likely to be higher near the propellant surface. The experimental setup is relatively new and the authors believe that they require better electrical insulation that will help produce better data for modeling efforts.

Cauty et al. pioneered the use of ultrasound transducers to measure solid propellant combustion response [69]. This technique has been transferred to studies in the United States and will be described in detail through the work of Murphy et al. and DiSalvo et al. [70,71,72,73].

Murphy et al. used an ultrasound and laser scanning system to measure both the steady state and transient burning rates of propellants [70,71]. They used a small end-
burning rocket motor that was fitted with windows for optical access. The propellant was placed on a pedestal to allow an ultrasound transducer to be fitted under the propellant. A tungsten rod was inserted into the rocket nozzle to achieve the pressure transient. The motor was tested at pressures up to 10.30 MPa. Figure 2-12 shows a schematic of the experimental setup.

Two bi-modal AP/HTPB propellants, manufactured by Thiokol Corporation, were used. Since this technique measures the instantaneous web thickness, considerable analyses and assumptions are required to obtain the steady state or transient burning rate. The steady state burning rate data for the non-aluminized propellant was compared against the quasi-steady burning rate calculated from the pressure and steady-state burning rate data provided by Thiokol. The comparison was in good agreement except at the beginning and end of the tests where the ultrasound data tended to overshoot. This may be due to actual burning rate oscillations or may be due to the data reduction technique. Comparison for the aluminized propellant also showed similar overshoots at the beginning and end of the combustion process.
Figure 2-12 Schematic of the Ultrasound system used to measure Burning Rate [70].
Transient burn rate data for both propellants were also compared against the quasi-steady data. The transient test for the non-aluminized propellant showed a rise along the quasi-steady curve up to about 14 atmospheres, and then lagged the curve as the pressure increased. The burn rate lagged the quasi-steady data by about 50 msec through the remainder of the experiment. Transient testing on the aluminized propellant showed the burn rate to lag the quasi-steady data during the initial pressurization and then catch up and then rises along the quasi-steady curve. The end of the combustion process once again showed large oscillations in the burn rate data. This may be an effect of the data reduction process. This experiment is still in its preliminary stages and requires further development to obtain data that can be related to combustion instability.

Di Salvo et al. have also used an ultrasound system to measure combustion response of a solid propellant [72]. Small propellant samples were tested in open and closed bombs to obtain burning rates during pressure transients. In the closed bomb tests, the propellants were burned in a chamber pre-pressurized with nitrogen. The exhaust gases cause the chamber pressure and the pressurization rate to increase. This test simulated “quasi-steady” burning of solid propellants over a large range of pressures. The open bomb tests were used to study the effect of transient chamber pressure. The pressure was modulated through periodic supply of nitrogen purge. An Aerotech propellant with 15% HTPB and 85% AP was used. The propellant was cast into a tube with a diameter of 1 inch (25.4 mm).

Analysis of the closed bomb pressurization rate showed that the quasi-steady assumptions are not valid particularly at the end of the test where the pressurization rates
are very high (1800 psi/sec ~ 122.45 atmospheres/sec). The burn rate results from five different closed bomb tests were curve-fitted and showed good consistency. The pressure exponent was measured to be 0.35 at 200 psia (14.6 atmospheres), and the burning rate was 0.23 inches/sec (5.8 mm/sec). The burning rates and pressure as a function of time were measured during the modulated tests. A predicted burn rate curve was also plotted. This predicted rate was determined by applying the experimental pressure to the burn rate curve fit. The calculated and measured burning rates showed the same general trend. The noise in the pressurization rate tended to affect the burning rate significantly and cause large uncertainties.

Di Salvo et al. applied the ultrasound technique to obtain a non-dimensional pressure-coupled response [72,73]. They used a vented chamber with pressures from 600-1200 psig (41.8-82.6 atmospheres). The frequencies ranged from 10-75 Hz. The periodic pressure oscillations were obtained by injecting inert gas into the chamber. Repeat testing at 10 Hz and 100 psig (7.8 atmospheres) produced response results that are claimed to be within 3%. The pressure-coupled response amplitude at about 1050 psig and 10 Hz is 1.05, and 24 Hz is 1.15. The phase shows a lag of 0.15 and 0.34 radians at 10 and 24 Hz respectively. The burn rate and pressure time traces show large fluctuations in the amplitude as well as mean values, which will significantly affect the phase information. The pressure-coupled response amplitude at about 600 psia (40.8 atmospheres) and 73 Hz is 2.05 and the phase shows a lag of 1.45 radians. The amplitude at 1230 Hz is 2.84 and the phase lags by 2.36 radians. The large phase lags are believed to be due to noise from the power grid. The power grid has a fundamental
at 60 Hz and harmonics at 30, 120 and 180 Hz. The fluctuations induced by the noise are of the same order as the burning rate fluctuations and clearly disrupt the amplitude and phase information. Isolation of the acquisition system is required to obtain reliable pressure-coupled response data.

### 2.2.3 Other Unsteady Measurements

Cardiff et al. also developed a numerical and experimental setup to obtain velocity-coupled distributed combustion response [74]. They performed cold flow tests and numerical modeling to show that the velocity-coupled distribution combustion magnetic flowmeter could generate the acoustics required to measure velocity-coupled distributed combustion response. The experimental setup was similar to the magnetic flowmeter burner with the addition of transverse acoustic forcing. This forcing is achieved by using piezoelectric acoustic exciters that operate 180° out of phase. These exciters provide a pure velocity oscillation in the middle of the chamber where the electrodes are located.

### 2.2.4 Temperature Measurements

Several uncertainties are associated with the use of thermocouples, though they are very useful tools to measure temperature. The uncertainties include radiative heat loss, conduction heat loss, catalytic effects, and thermal inertia effects. To obtain accurate temperature profiles, the uncertainties must be corrected. A detailed discussion for the uncertainties is given below.
Bradley and Matthews [75] investigated the heat conduction loss through the thermocouple wires for measurement of high gas temperature. To estimate the heat loss through conduction, the energy equation was solved for a semi-infinitely long Pt/Pt-10 % Rh wire. The wire with a support temperature of 300 K was 0.0005” in diameter in gas mixtures of 600 K, 1300 K and 2100 K. The profiles showed that the thermocouple was not substantially affected by conduction cooling, if each component wire had a length of at least 0.125 in. A shorter wire length results in cooling of the junction due to heat conduction along the wires. Care should be taken in selecting the necessary thermocouple wire length in order to prevent conduction heat losses. Heitor and Moreira [76] proved that conduction heat losses were negligible for length-to-diameter rations above 200.

Surface catalysis on the uncoated thermocouples can cause large errors. Cookson, Dunhan, and Kilhan [77] measured temperatures in an 18 % hydrogen-air flame by using Pt/Pt-13% Rh thermocouples. Significant errors were observed due to catalytic heating. Heitor, Taylor, and Whitelaw [78] found catalytic effects were of secondary importance in the turbulent flame. Measurements have been made to study the effects of catalysis by Thomas and Freeze [79]. Pt/Pt-13% Rh thermocouples were used to measure the temperature of incompletely burned gases in the temperature range from 1000 to 1500°C. Pt/Pt-13% Rh thermocouple elements were exposed to gas mixtures of air + 1.0 % H₂, air + 2.0 % H₂, air+1.0 % CO + 0.01 % H₂, air +2.0% CO +0.01% H₂ and air +0.5% C₄H₁₀. At very low gas velocities, surface catalysis caused an error in the thermocouple temperature from about 2 to 77°C at thermocouple temperatures between
1000 and 1500°C. At gas velocities between 17 and 183 m/sec, the temperature increased and varied between 35 and 380°C.

Large errors may result from radiative heat exchange between the thermocouple and surroundings. For example, for a 40 µm thermocouple the error was as high as 150°C in a premixed flame of methane and air [80]. Bradley and Matthews [75] assumed that the surrounding walls were black to radiation from the wire and radiation energy exchange between the wire and the gases was negligible. The steady state energy equation for an uncoated wire can be written as follows:

\[
\frac{d}{dx} \left( k \frac{dT}{dx} \right) + \frac{4h}{D} (T_b - T) - \frac{4\sigma}{D} (\varepsilon T^4 - \alpha T_b^4) = 0
\]  

(2.21)

where \( h \) is convective heat transfer coefficient, \( k \) is thermal conductivity, \( \sigma \) is Stefan-Boltzmann constant, \( \varepsilon \) is wire emissivity, \( \alpha \) is wire absorptivity \( T_b \) is environmental temperature, \( T_G \) is gas temperature and \( T \) is wire temperature. If the thermal conduction along the wire is negligible, the first term can be dropped. In practice, for wire temperatures above 1000°C and low wall temperature the absorption term \( \alpha T_b^4 \) is usually negligible. The equation can be written as

\[
T_G = T + \frac{\sigma \varepsilon T^4}{h}
\]

(2.22)

The uncertainty in equation (2.22) is high due to the lack of knowledge of the local convective heat transfer coefficient. In addition, there is no reliable data available for the emissivity of platinum alloys.
Errors in measurement may also arise due to the thermal inertia of a thermocouple. A correction must be made for the time dependent temperature measurements[81]. To simplify the problem, the conduction and radiation heat losses from the thermocouple, as well as any catalytic effects on its surface are neglected. The energy equation can be written as follows:

\[
T_g = T + \tau \frac{dT}{dt}
\]  
(2.23)

where \( \tau = \frac{\rho C_p V}{Ah} \) is the characteristic time constant of the thermocouple, \( h \) is local heat transfer coefficient, \( A \) is area, and \( V \) is volume. Based on this equation, the corrected temperature can be readily obtained as long as the time constant is known.

### 2.2.5 Measurement of Thermo-Physical Properties

Parr and Hanson-Parr studied the thermal properties and gas phase flame structure of AP/HTPE and AP+AN/HTPE propellants [82]. Three propellant formulations were used. TP1 and TP2 had 70% AP and 10% AN, TP3 had 80% AP. TP2 had fine AN, while TP2 had coarse AN. The authors used a thin foil that was electrically pulsed and heated one side of the propellant. A 5 \( \mu \)m thermocouple was placed on the opposite face to detect the heat pulse. The system was sealed in a heat box to measure the sample properties as a function of temperature. The thermal diffusivity of all three propellants was about \( 1.555 \times 10^{-3} \) cm\(^2\)/sec. The thermal diffusivities for the three propellants showed minor changes with an increase in temperature. The heat capacity for the three propellants was about 0.25 cal/gm\(^\circ\)C. The study showed that there are no differences in
thermal properties between the three propellants. The authors used a 150 Watt CO\textsubscript{2} laser to record ignition properties. They used the gas phase flame ignition point as a reference to calculate the ignition delay. For all three propellants, the ignition delay decreased from 200 ms at 20 W/cm\textsuperscript{2}, to 20 ms at 600 W/cm\textsuperscript{2}. The authors also used 5, 13 and 25 \( \mu \)m type K thermocouples to measure the condensed phase thermal profiles. The profiles were measured at 1 atmosphere and had large standard deviations in the surface temperature. This is due to thermal lag and lead loss effects. The condensed phase temperature profiles showed a shallow slope far from the surface turning sharply into a steep slope close to the burning surface. The surface temperatures for TP1, TP2 and TP3 were 800, 1050 and 1100 K respectively. The different surface temperatures were attributed to differences in the condensed phase decomposition behavior. The gas phase flame structure was measured through Planar Laser Induced Fluorescence (PLIF) of OH radicals. The measurement technique provided two dimensional images of OH concentration and gas temperature. The authors found no significant differences in gas phase temperatures and OH concentrations during laser assisted combustion of the AP and AP+AN propellants. The flame temperatures were 2900 K at 1 atmosphere. The temperature was higher than the adiabatic flame temperature due to external laser heating.
Chapter 3

EXPERIMENTAL APPROACH

This chapter describes the experimental facilities for laser and pressure-driven combustion response measurements. The facilities are located in the CO$_2$ laser laboratory of the Department of Mechanical and Nuclear engineering at The Pennsylvania State University. Section 3.1 describes the setup for the laser-driven combustion studies of propellants. Section 3.2 focuses on the experimental procedure and data reduction methods used during laser-driven combustion. Sections 3.3 and 3.4 describe the development of the setup and instrumentation and the experimental procedure and reduction and validation techniques used for pressure-driven response measurements. Section 3.5 describes the setup for temperature measurement under steady-state conditions.

3.1 Setup for Laser-Driven Response Experiments

This section describes the experimental setup that has been used for measurements of burning rate, light emission, and luminous flame height response to sinusoidal laser heating. A Synrad CO$_2$ laser, a Kistler micro-force transducer, and HgCdTe detector
with related electronics were initially installed and subsequently modified to ensure reliable unsteady measurements.

### 3.1.1 CO₂ Laser System

A schematic of the setup for laser-driven response measurements is shown in Figure 3-1. A Synrad 57-2 CO₂ laser is used as a heating source to ignite the propellant and generate oscillatory combustion. The laser, governed by appropriate control signals, could provide a nearly sinusoidal heat flux of up to 200 W at frequencies up to 1000 Hz. A Synrad laser controller, model UC-1000 is used to modulate the laser. In addition to providing the appropriate driving signals, the controller also provides a 1 µs tickle pulse to the laser. This tickle pulse is necessary because without it the laser response time will vary from 10 to 100 µs. The variation in response time is due to the time required to create plasma within the laser tube. The tickle signal pre-ionizes the gas to just below the threshold level and provides a controlled response time lag of 100 µs. This allows the laser to respond predictably and instantaneously to the user input.

A programmable voltage source (Hewlett Packard programmable universal source, HP-3245A) was used to generate the required waveforms for laser-driven combustion. The system provided flexibility in selecting the specific frequency and frequency duration. The sinusoidal control signal generated by the computer-controlled HP-3245A universal source was converted to a pulse train at 5 kHz through the UC-1000 laser controller. The laser beam had a nearly Gaussian energy distribution (mode quality greater than 90% TEM₀₀) and was combined with a visible diode beam right at the CO₂
laser output for purposes of beam alignment. The beam was then divided into two beams through a germanium beam splitter. The beam splitter was purchased from Laser Optics Inc., and was designed for use at an incidence of 45° and a wavelength of 10.6 µm. The beam with 99.5% of CO₂ laser power passed through a zinc selenide expanding lens and a potassium chloride window before entering the test chamber. The zinc selenide lens provided a relatively uniform beam with a 10-15% variation across the area of interest. The expanding lens was mounted on a sliding mount movable along the track directly above the chamber. By varying the distance between the selenide lens and the sample surface, different levels of mean incident heat flux could be obtained. The average heat flux was measured by a calorimeter bought from Optical Engineering, which was masked by a copper plate with an aperture of 5 mm. Thus, heat flux was measured at the center 5-mm diameter portion of the entire beam. The remaining 0.5% energy was passed to a HgCdTe power detector (Boston Electronic PEM-L-3). This sensitive power detector was used to monitor the waveform of the laser power as a function of frequency. Appendix C shows the block diagram of the power detector with related electronics. The wiring diagram for the laser-driven combustion experiments is presented in Appendix D.
Figure 3-1 Overall experimental setup for Laser-Driven Response Measurements
Figure 3-2 shows the typical output waveforms for the laser and laser controller [83]. The laser controller output was a square wave train at a frequency of 5 kHz. Since the output of the laser followed the clock input with a time constant of approximately 100 µs, the laser output was no longer a square wave train. This is clearly visible in figure 3-2.

The laser output power varied approximately linearly with the length of duty cycle in output pulses from the laser controller. The HgCdTe detector with related electronics allowed measurement of laser output power. Thus, a comparison could be made between the control signal and laser output power. The measured results indicated that the laser did not precisely follow the control signal supplied by the Hewlett Packard universal source. Figure 3-3 shows the amplitude and phase relationships between the control signal and laser output power. The measured data was corrected for these amplitude and phase errors during data analyses.

![Wave forms for the outputs of the laser and laser controller](image-url)
Figure 3-3: The amplitude and phase relations between the laser output and control signals
3.1.2 Test Chamber

The test chamber displayed in Figure 3-4 is 28 cm tall and 20.5 cm wide with aluminum walls that are 1.3 cm thick, resulting in an internal volume of 8138 cm$^3$. A micro-force transducer was installed vertically in the bottom wall through an M10 threaded hole. Since the transducer was very sensitive to changes in pressure, a slight pressure change generated by gas production during combustion of the propellant sample could cause a large error in the measured thrust data. To minimize the variation of pressure within the test chamber, several holes with a diameter of 9.5 mm were drilled
into the bottom wall to vent it to atmosphere. A mechanical pump was connected to the top wall. During a test, the pump continuously removed gas from the chamber; thus, all the toxic gas products went into the exhaust vent.

An aluminum enclosure was designed to protect the transducer from laser heating, hot combustion gas products, and particulates generated by combustion of the propellant sample. A plexiglass window, 0.64 cm. in thickness, was installed on one side of the chamber to allow video recording of the combustion event. Three openings 10 cm in diameter were located on the other three sides of the chamber to allow access to the sample holder. The three openings were sealed after the sample was installed into its assembly. As mentioned in an earlier section, the CO₂ laser beam entered the test chamber through a potassium chloride (KCl) window.

3.1.3 **Diagnostic Systems**

3.1.3.1 **Micro-force Transducer and Charge Amplifier**

A Kistler 9207 high-sensitivity micro-force transducer, mounted inside an aluminum enclosure, was used to measure instantaneous thrust. The transducer was very sensitive to changes in temperature, excessive vibration, and variation in pressure. The propellant sample was glued to a threaded pedestal that was made from aluminum. The pedestal was screwed into 4-40 threads on the micro-force transducer. To reduce unwanted vibrations, the length of the pedestal was made as short as possible. The transducer had a
sensitivity of 113.6 pico-coulombs/Newton. The natural frequency for the transducer setup was determined to be 10 kHz by suddenly imposing a force on the transducer. Since test frequencies were all below 1 kHz, the thrust signals were not affected by the natural frequency of the transducer setup.

A Kistler type 5010 charge amplifier amplified the thrust output signal. A 1 kHz low-pass filter was connected to the charge amplifier to filter out unwanted high frequency noise. The amplifier was also set to have a sensitivity of 113.6 Pico Coulombs/Newton and provided an output of 0.01 Newton/Volt. Appendix E details the calculations that were performed to eliminate the probability of photons of energy from the CO₂ laser imparting momentum onto the force transducer.

### 3.1.3.2 Combustion Photography

A Pulnix TMC-7 CCD camera with a micro lens was used to obtain images of the flame structure. The images were recorded on a BV-1000 Mitsubishi VCR. The VCR had a jog/shuttle feature that allowed the images to be reviewed on a frame-by-frame basis. A Nikkor micro lens with a focal length of 60 mm was purchased from Nikon. The combination of the lens and camera provided a maximum magnification of over forty times the actual size, which gave a spatial resolution of 25 μm. The camera recorded color images and had a maximum recording speed of 30 pictures per second (pps).
3.1.3.3 Other Instrumentation

A near-infrared photodiode with an amplifier circuit was used to monitor visible/near-IR emission from oscillatory combustion of the propellant sample. The amplifier circuit, made in-house, was used to increase the signal to noise ratio. The sensor was located 8 cm above the propellant surface and 4 cm from the laser beam centerline with the photodiode’s optical axis aimed at the propellant surface. The emission was recorded on an oscilloscope and was used to determine the combustion response of light intensity.

A red LED was installed in the chamber to determine the laser trigger time on the video image. The LED emitted red light once the laser was triggered. Thus, the first video image with the red light indicated the starting time of laser heating.

An IBM PC based 80486 computer with a high-speed I/O board, and an analog oscilloscope were some of the data acquisition devices that were used. The board with 16-bit output resolution was capable of a maximum sampling rate of 100 kHz. The board could obtain four A/D inputs at the same time and allow simultaneous output of analog signals through two D/A channels. In the current setup, one of the D/A channels was used to trigger the \( \text{CO}_2 \) laser.

A two channel, Nicolet 310B, digital oscilloscope, was used to record the thrust response and laser control signal. The additional signals were recorded on an IBM based Pentium-II PC using a 16 bit data acquisition card. The acquisition card, model PC-MIO-16XE-10, was purchased from National Instruments, Co. and allowed storage of up to 16 (8 differential) channels of data. This data acquisition board was also capable of sample
3.2 Experimental Procedure

3.2.1 Setup and Data Collection

At the start of the test, the 80486 computer triggers the laser and the data acquisition on the Nicolet 310B digital oscilloscope. Graphics programming through the Labview software allowed the data acquisition on the Pentium-II computer to be triggered by the laser trigger signal. This allowed simultaneous collection of data on all acquisition systems. During the test, high magnification video images are also taken so that the average burning rate can be determined and any abnormalities in the data traces can be compared to the video images.

Before each combustion response measurement, the amplitude, mean value, and frequencies of heat flux were programmed through DA5, an in-house, data control, computer program, written by a previous Ph.D. student [84]. The exhaust pump was first turned on to prevent an increase in chamber pressure during the response measurements. The charge amplifier was set to its highest gain to check for noise. During loading of the propellant samples, the amplifier was placed into the reset mode due to the fact that a small level of vibration could easily cause amplifier overload. Just before triggering the laser, the amplifier was switched back to the operate mode.
The data on the oscilloscope was stored onto a floppy disk. VU-Point software purchased from Nicolet was used to convert the data into text format. This text-formatted data was then converted into an EXCEL spreadsheet. The data recorded on the Pentium-II PC was stored on a designated hard disk drive in text format. This file was also converted and analyzed using Microsoft EXCEL.

### 3.2.2 Data Reduction

Special data reduction procedures had to be followed for laser-driven combustion of the heterogeneous AP composite propellants. These propellants had a typical burning rate of 1.7 mm/sec at one atmosphere. Due to this comparatively higher burning rate, the thrust response data from the force transducer showed a downward trend due to the large mass consumption rate.

Figure 3-5 shows a typical thrust-time trace for a MURI propellant during laser-driven combustion. The transducer measures a momentum flux \( \rho_p v^2 \), and the thrust signal shows a large slope due to this higher mass consumption rate. This large slope affects the amplitude and phase response data at low frequency. To avoid this inaccuracy, the slope is mathematically eliminated from the thrust-time trace. Figures 3-6 and 3-7 show the corrected and uncorrected time traces for MURI 5 during laser-driven combustion at one atmosphere. The results of a Fast Fourier Transform of both time traces are shown in Table 3-1. The alteration of the thrust signal did not have a significant influence on the amplitude, but clearly affected the phase information. The
uncorrected thrust data showed a phase lag of 4.1 degrees, but the corrected thrust data showed a phase lead of 16.1 degrees.

<table>
<thead>
<tr>
<th>Thrust-time trace</th>
<th>Amplitude (mN/Watt)</th>
<th>Relative Phase (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrected</td>
<td>0.012</td>
<td>16.1</td>
</tr>
<tr>
<td>Uncorrected</td>
<td>0.010</td>
<td>-4.1</td>
</tr>
</tbody>
</table>

Table 3-1: Amplitude and Phase response data for laser-driven combustion of MURI5 at one atmosphere.

![Thrust Time trace during laser-driven combustion of MURI5 at 1 atmosphere.](image)

Figure 3-5 Thrust Time trace during laser-driven combustion of MURI5 at 1 atmosphere.
Figure 3-6 Uncorrected Thrust-time trace for combustion of MURI5 at one atmosphere.

Figure 3-7 Corrected Thrust-time traces for combustion of MURI5 at one atmosphere.
3.3 Setup for Pressure-Driven Response Measurements

This section describes the experimental setup that has been developed for measurements of pressure-driven combustion responses of burning rate, light emission, and luminous flame height. The Synrad 57-2 CO₂ laser, a Copper Instruments Co. subminiature load cell, and a Validyne pressure transducer with related electronics were used to make pressure-response measurements.

3.3.1 Synrad CO₂ Laser System

The Synrad 57-2 CO₂ laser is used to ignite and sustain combustion of the propellant samples. A potentiometer is used to control the laser output power. The potentiometer is connected to the UC-1000 laser controller through the ANV/C control pod. The ANV/C control pod allows remote control of the CO₂ laser output through a voltage or current source. The potentiometer provides a constant output in volts to the laser controller. This results in a constant laser output. This is distinctly different from the procedures used during laser-driven combustion.

As mentioned in an earlier section, the laser beam had a nearly Gaussian energy distribution and was combined with a visible diode beam right at the CO₂ laser output for purposes of beam alignment. The combined beam passed through a germanium beam splitter, a zinc selenide expanding lens and a KCl window before entering the test chamber. Changing the voltage input from the potentiometer to the ANV/C control pod on the laser controller varied the average heat flux. Unlike the laser-driven tests, the zinc selenide lens was kept at a fixed reference position on the movable mount. The average
heat flux was measured by a calorimeter bought from Optical Engineering, which was masked by a copper plate with an aperture of 5 mm.

**3.3.2 Test Chamber and Pressure Driving System**

Figures 3-8, 3-9 and 3-10 show schematics of the test chamber used during pressure-driven combustion. During experiments, two model airplane engines driven by an AC motor produce nearly sinusoidal pressure variations, with a peak-to-peak variation of 10 % (\(\Delta P/\bar{P}\)). To achieve this relatively high variation in ambient pressure, there were design limitations in selecting the volume of the test chamber and the specification of the model engines. The design target of the driver was to have a \(\Delta P/\bar{P}\) of 10 % regardless of the chamber pressure and excitation frequency. Although a model engine operating up to a RPM of 30,000 (frequency of 500 Hz.) was available, its displacement volume was too small to achieve the target \(\Delta P/\bar{P}\) with a reasonable chamber volume.
Figure 3-8 Schematic of the experimental setup used for Pressure-Driven Combustion
Figure 3-9 Schematic of the test chamber used for Pressure-Driven Combustion
To obtain the target pressure variation, and construct a test chamber with a reasonable chamber volume, the model engine selected was model BGX-1 engine, manufactured by the O.S. Engine Co. The engines had a maximum possible excitation frequency of 167 Hz and a displacement of 34.97 cm³. The specifications of the engine are listed in Table 3-2. The desired test chamber volume was calculated to be about 700 cm³, corresponding to a cubic chamber with each side 9-cm (3.55”) in length. The cylinder heads of the engines were removed, and the engines were attached to opposite sides of the test chamber by using the threads on the top of the cylinder block. Since the focus of this study is pressure-driven unsteady combustion, the engines were set to be 180° out of phase. Therefore, only pressure variations are present near the surface of the
propellant sample and the flame. To prevent the effect of any gas flow inside the chamber on the burning surface and flame of the propellant, the sample was placed at the center of the chamber.

The original engine was supposed to run with the two-stroke cycle; therefore, its cylinder liner (sleeve) had ports on its side for intake and exhaust. To obtain nearly sinusoidal pressure variations without pressure leakage during tests, a new sleeve without the holes was built to replace the original sleeve. An encoder was attached to one engine to identify the relative position of the piston.

To the end of each engine crankshaft, a timing belt pulley was attached with a taper bushing. The pulley and bushing were also attached to the shaft of an AC motor so that the one timing belt connected all three pulleys. Various frequencies of pressure variation were achieved by changing the piston speed of the engines through the timing belt and the AC motor. Since the AC motor runs the model engines, the maximum power required for the motor was calculated based upon the maximum pressure during a test and the cylinder wall friction. Since there were no available data for the friction force, it was estimated using data for larger engines near the maximum speed of the engine [85]. The selected motor has a maximum power of 5 HP at 3500 RPM (~60 Hz) and supplied various frequencies to the model engines through variation of an input voltage that controlled frequency from zero to 60 Hz through an AC inverter. Both the AC inverter and motor were purchased from Grainger Inc.

In order to observe the presence of any non-linearities associated with the harmonics of the driving frequencies of the airplane engines, pressure traces were collected and analyzed. Figure 3-11 shows a plot of the square of the amplitude of a Fast Fourier
Transform on the pressure within the combustion chamber. The trace was collected during pressure-driven combustion experiments on a MURI propellant at one atmosphere. The figure clearly shows that most of the power is delivered at the driving frequency of 8 Hz. A harmonic is observed at 16 Hz, but is four orders lower in magnitude. There is substantial noise observed at the lower frequencies and that is believed to be an artifact of the Fast Fourier Transform technique coupled with some low frequency vibrations. This figure justifies the assumption that the airplane engines deliver a nearly sinusoidal pressure variation.

3.3.3 H-Beam Assembly

The motor was fixed on an adjustable stand and the combination of the test chamber and engines were fixed onto a steel plate and H-beam assembly to absorb excessive engine vibrations. Figure 3-12 shows a detailed drawing of the H-Beam assembly.
Figure 3-11 Fast Fourier Transform of the Chamber Pressure during combustion of an MURI propellant at one atmosphere.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement</td>
<td>43.97 cc</td>
</tr>
<tr>
<td>Bore</td>
<td>37.3 mm</td>
</tr>
<tr>
<td>Stroke</td>
<td>32.0 mm</td>
</tr>
<tr>
<td>Practical RPM</td>
<td>1,500 – 10,000</td>
</tr>
</tbody>
</table>

Table 3-2: Specifications for the model airplane engines
The H-beams were bolted to the floor and tested with shock loading to determine their natural frequency. The largest response from the assembly was detected at ~ 450 Hz. The maximum frequency of the airplane engines was limited to 130 Hz and hence the resonant frequency of the assembly was not an issue.

Despite the use of H-Beams, vibrations of the test chamber could not be entirely eliminated. GP-DS visco-elastic damping material, obtained from BPG Inc., was used to connect the ceramic thermal protector to the bottom of the test chamber. The damping material significantly reduced the vibrations and allowed a minimum signal to noise ratio of 3:1.

3.3.4 Devices for Thrust Measurement

Data acquired in experiments include thrust from a load cell, pressure trends from a pressure transducer, and light emission signals from a photo-diode. This sub-section will focus on the devices used in the thrust response measurement system.

3.3.4.1 Sub-miniature load cell

During propellant combustion, thrust response was measured using a sub-miniature load cell. Due to the small test chamber volume, a pressure increase from one to two atmospheres was experienced during experiments.
In order to prevent the transient chamber pressure from affecting the thrust data, a pressure insensitive sub-miniature load cell, LPM510, was purchased from Cooper Instruments Company. The load cell has a maximum capacity of 150 grams under compression and uses a strain gage cantilever beam mechanism to measure burn rate response. The sub-miniature load cell requires an external excitation DC voltage of 5 volts. The load cell has a full-scale range of 11.08 mV/Volt of the excitation signal and
produces an output in the range of 0.1–0.15 mV per excitation input voltage and gram weight. Therefore, a voltage amplifier was used to amplify the output signal; a gain of 500 to 1000 was normally adopted in experiments. The amplifier will be discussed in a later section.

On the authors’ request, Cooper Instruments Co. drilled a vent hole along its bottom surface to allow the ambient pressure to be simultaneously applied on the top and bottom sides of the sensing element. This ensured pressure-insensitivity of the load cell.

3.3.4.1.1 Thermal Protector

During combustion, the temperature of the ambient gas within the chamber was as high as 300°C. The sub-miniature load cell can be safely operated at temperatures ranging from room temperature to about 71°C (160°F). Due to the high temperature gases within the combustion chamber, the load cell was placed in a low conductive ceramic thermal protector.

Figure 3-13 shows a schematic of the thermal protector. The thermal shield consisted of two halves joined together by four 4-40 screws. The shield had an outer diameter of 1.2” and the walls were 0.3” thick. The load cell was glued to the bottom half of the protector and was loaded through a hole and an adapter assembly in the top half. The sub-miniature load cell had a pressure vent along its bottom surface and hence a channel was created in the bottom half of the thermal protector to allow the load cell to vent. Temperature measurements within the load cell protector showed that the maximum temperature during combustion never exceeded 46°C (115°F).
3.3.4.1.2 Adapter Assembly

An adapter assembly was created to ensure accurate and repeatable loading of the load cell. Figure 3-14 shows a schematic of the adapter assembly. A ceramic buffer was fitted onto the load cell through the hole in the top half of the thermal protector. A through hole was created in the buffer and an aluminum pedestal was glued into the buffer. A tip on the bottom of the aluminum pedestal helped center it into the buffer. The propellant sample was glued into a quartz vial, which was then glued to a 4-40 threaded rod that was screwed into the aluminum pedestal.

After each test, the rod and vial were removed and the quartz vial was replaced. This approach eliminated the need to remove the thermal protector assembly and reduced the down time between tests. The adapter elevated the near-surface combustion zone and the burning surface of the propellant sample to the centerline of the two model airplane engines. Since the height of the ceramic shield matches the adapter assembly, possible fluid motion effects on the sample due to the movement of the pistons is minimized.
Figure 3-13 Drawing of the Thermal Protector used during Pressure-Driven Combustion
3.3.4.2 Differential Amplifier

To amplify the signal from the sub-miniature load cell, a differential amplifier, model 428, from Ectron Corporation, was purchased. The Model 428 conditioner-amplifier is a chopper stabilized differential DC amplifier that can provide an excitation voltage supply. The amplifier has an output range of ±10 Volts and can provide a continuous gain from 0.1 to 2500. The amplifier also supplies the 5 volts required to
excite the sub-miniature load cell. The amplifier gain was set to 500 or 1000 depending on the test conditions.

### 3.3.4.3 Differential Pressure Transducer and Demodulator

A differential pressure transducer was obtained from Validyne Engineering Corporation. The transducer used a pressure-sensing diaphragm to measure the unsteady ambient pressure within the combustion chamber. The diaphragm has a range of ±30 psid. The DP15TL transducer had one side of its diaphragm exposed to the atmosphere while the other side measured the excitation pressure oscillations produced by the model engines, as well as the change in average chamber pressure. The transducer was purchased with seven other diaphragms and has a pressure range from ±1, to ±3000 psid. This allows the transducer to be used at all our test conditions. The transducer has very few moving parts and is highly resistant to shock and vibration. The frequency response of the transducer is high (greater than 10 kHz). The transducer is connected to a carrier demodulator, Model CD12, which was also purchased from Validyne Engineering Corporation. The demodulator amplified the transducer output and provided the required transducer excitation. It also has a built in low pass filter at 1000 Hz that was used under certain test conditions. The differential output from the demodulator was connected to the two channel digital oscilloscope.

### 3.3.4.4 Other Instrumentation

As mentioned in an earlier section, a near-infrared photodiode circuit was used to monitor visible/near-IR emission from oscillatory combustion of the propellant sample.
The sensor was located above the propellant surface with the photodiode’s optical axis aimed at the propellant surface. The emission was recorded in the scope and was used to determine the combustion response of light intensity.

Additional devices for processing signals included the IBM PC based 80486 computer with a high-speed I/O board, and an IBM PC based Pentium II also equipped with a data acquisition card. In the current setup, one of the D/A channels on 80486 computer was used to trigger the CO₂ laser.

A two channel, Nicolet 310B, digital oscilloscope, was used to record the thrust response and laser control signal. The additional signals were recorded on the IBM based Pentium-II PC. Data collection and analyses on the Pentium II computer was performed using Labview.

A Pulnix TMC-7 CCD camera with a micro lens was once again used to obtain images of the flame structure. The images were recorded on the BV-1000 Mitsubishi VCR.

The outputs from the load cell and the pressure transducer were connected to individually foil-shielded, twisted-pair, insulated cables. The radio frequency power source of the CO₂ laser caused a large disturbance in the output signals. Isolation of the cables through twisted pair cables dramatically reduced the noise.

### 3.4 Experimental Procedure

#### 3.4.1 Setup and Data Collection
Before combustion, the quartz vial is loaded with the propellant sample. The vial is glued to an aluminum pedestal, which is fitted into the adapter assembly and placed in the combustion chamber. A new layer of GP-DS visco-elastic damping material is applied to the bottom of the thermal protector assembly. Light pressure is applied to ensure a tight fit. The combustion chamber was then sealed, the airplane engines were turned on at the required excitation frequency and the load cell response was measured. This response provides an indication of the pressure sensitivity of the system. In an effort to ensure accurate and reliable data, the load cell signal was collected before, during and after combustion of each propellant sample. The signal is collected on the digital oscilloscope and analyzed through an Excel spreadsheet. A Fast Fourier Transform is performed on this data and the intensity is compared to the response during combustion. Figure 3-15 shows a typical plot of the Fast Fourier Transform of the load cell data before and during combustion. The real time response amplitude had this signal subtracted from it to give the real thrust response. This pressure sensitivity results in a higher degree of uncertainty in the phase data.

At the start of each test, the 80486 computer triggers the laser and the data acquisition on the Nicolet 310B digital oscilloscope and the Pentium-II computer. During the test, high magnification video images are also taken through the macro lens and the VCR so that the average burning rate can be determined and any abnormalities in the data traces can be compared to the video images.

The photo-diode was placed at an upper corner of the test chamber to detect the visible light emission from the flame of a sample propellant. The signal response from it was analyzed to compare with the thrust response profiles. The unsteady pressure
oscillation detected by the DP15 differential pressure transducer was recorded on the
digital oscilloscope.

Thrust response and pressure signals were stored in a storage oscilloscope at a rate of
1000 samples per second. The relatively low sampling rate was used due to memory
restrictions on the oscilloscope. The sampling rate was still considerably higher than the
maximum excitation frequency of 96 Hz. The photo-diode signal was recorded at 2000
samples/sec on the Pentium-II based IBM PC.

Fast Fourier Transform analyses were used to obtain amplitude and phase
information from thrust response profiles. Fast Fourier Transform analysis was
performed using a spreadsheet (Microsoft Excel) or a computer program. The Fast
Fourier Transform function in Excel can process only 1024 data points while the in-house
computer program could process 4096 points. A low-pass software filter was used to
filter out the high frequency noise above 500 Hz. The amplitude and phase data for thrust
response were compared with those for pressure excitation signals. This allowed
measurement of a dimensional thrust response that includes amplitude and relative phase.
Figure 3-15 Typical results from a Fast Fourier Transform of the load cell signal before and during combustion

3.4.2 Data reduction

During pressure-driven combustion of the homogeneous as well as heterogeneous propellants, the ambient pressure rose from its initial value of one atmosphere to about two atmospheres. Figure 3-16 shows a typical thrust and pressure-time trace during pressure-driven combustion. The airplane engines were driven at a single driving frequency of 8 Hz during this test. The thrust signal is similar to the laser-driven combustion experiments and shows a steady decrease due to mass consumption. Data reduction for these pressure-driven tests is further complicated by the increase in ambient
pressure. In order to obtain accurate amplitude and phase information, the mass consumption rate and pressure rise rate were obtained through a least squares fit and deleted from the thrust and pressure time traces.

Figure 3-17 shows the corrected thrust vs. time signal for combustion of MURI5, while Figure 3-18 shows the corrected thrust and pressure vs. time signals. The elimination of these consumption and rise rates allowed a more accurate determination of amplitude and phase information at low driving frequencies.

Table 3-3 shows the response values for the corrected and uncorrected signals. During pressure-driven combustion, the corrected thrust response amplitude also differs significantly from the uncorrected values. The laser-driven tests observed an effect only on the phase. This is probably a result of the increase in the ambient pressure coupled with the mass consumption of the propellant sample.

<table>
<thead>
<tr>
<th>Thrust-time trace</th>
<th>Amplitude ($R_p$)</th>
<th>Relative Phase (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrected</td>
<td>0.97</td>
<td>10</td>
</tr>
<tr>
<td>Uncorrected</td>
<td>0.80</td>
<td>-14</td>
</tr>
</tbody>
</table>

Table 3-3 Amplitude and Phase response data for Pressure-Driven combustion of MURI5 at one atmosphere.
Figure 3-16 Thrust and Pressure-time trace during combustion of MURI#5 at an initial pressure of one atmosphere.
Figure 3-17 Corrected load cell and uncorrected pressure signals during combustion of MURI5 at one atmosphere.
Validation of the test facility was a vital step in the development of an apparatus to measure pressure-driven combustion response. In order to achieve this goal, the MURI#5 propellant was chosen. This propellant sample was subjected to laser-driven combustion experiments in both the laser and pressure-driven combustion facilities. The propellant sample was subjected to identical initial test conditions and its response was measured using different diagnostic tools in different test chambers. The laser-driven combustion

Figure 3-18 Corrected load cell and pressure signals during combustion of MURI5 at one atmosphere.
facility has been used extensively for the past few years and worked as a benchmark in this process of validation. Similar response measurements for the MURI#5 propellant in the two test rigs will validate the diagnostic tools used in the new pressure-driven test chamber.

The propellant was tested at one atmosphere in air with an incident heat flux of 35 W/cm$^2$. The test frequencies ranged from 4 to 250 Hz in discrete steps. Figure 3-19 shows the dimensional thrust response for MURI#5 during laser-driven combustion at an incident laser heat flux of 35 W/cm$^2$. The solid symbols indicate the thrust response to laser-driven combustion in the laser-driven chamber. The open symbols are the thrust response to laser-driven combustion in the pressure-driven chamber. The measurements in the pressure-driven test facility are higher than in the laser-driven test chamber. The maximum amplitude is 1.97 E-5 N/W in the pressure-driven facility and is 1.8 E-5 N/W in the laser-driven chamber. The response shows a maximum at 16 Hz in both chambers.

During combustion, the ambient pressure in the pressure-driven chamber increases from 1 to 2 atmospheres. This pressure increase increases the mean burn rate and the amplitude of the oscillatory burn rate. This increases the thrust response in the pressure-driven chamber. The figure shows that the thrust response to heat flux using the pressure insensitive load cell in the pressure-driven combustion chamber compares extremely well to the thrust response data from the piezo-electric transducer in the laser-driven chamber. The figure also shows that the thermal protector and adapter used to protect the load cell in the pressure-driven test chamber do not hamper the process of data acquisition.
3.5 Temperature Measurement

The system for temperature measurement included fine wire thermocouples, a preamplifier, an oscilloscope, and a computer. Signals generated from thermocouples were recorded on a Nicolet 310 digital oscilloscope through a six-channel wideband preamplifier with a gain of 50 dB. The oscilloscope was triggered along with the CO2 laser by a signal output from the computer. The oscilloscope operated at a maximum recording speed of 1 MHz and had two input channels. Two 3.5” disk drivers were included for signal recording. The system recorded the data on the disks in DOS-compatible format so that they could be directly used in a computer. The data was
transferred to TEXT files by a VU-POINT software package. The conversion from voltage to temperature was based on the formula published by the Omega Company [87]. The conversion was processed by an EXCEL software package. Then the signals were corrected for the effects of thermal inertia based on equation 2.23.

Fine wire thermocouples, including Pt-Pt 13% Rh, Chromel/Alumel, and W-3%Re/W-25%Re, were used to measure temperature from the subsurface to the post flame. The Pt-Pt 13% Rh and W-3%Re/W-25%Re thermocouples were carefully welded together under a microscope to obtain the bead size as small as possible. A detailed procedure for making thermocouples is discussed in reference [88]. The Chromel/Alumel thermocouples with a diameter of 25 µm were directly purchased from Omega Engineering, Inc. When spatial resolution and temporal response were critical, the bead was rolled to a thickness under 10 µm using a roller. Then these thermocouples were reshaped into a “U” by a knife to minimize the heat loss through heat conduction.

Three different methods used in temperature measurements are shown in Figure 3-20. In the region from the subsurface to 1 mm above the surface, the U-shape thermocouples were embedded into the sample. The thermocouples were rolled to a thickness under 10 µm to obtain better spatial resolution. In the region from 0.5 mm above the surface, to the post flame, the W-3%Re/W-25%Re thermocouple with its leads protected by a ceramic tube was used. The thermocouple with a diameter of 75 µm was chosen to increase the lifetime of the thermocouple. The thermocouple was placed above the surface of the pellet. During a test, the sample was pulled away from the thermocouple by the linear positioner to obtain a temperature profile. Figure 3-20 also
illustrates the configuration for measurement of the surface temperature. The thermocouples were placed across the propellant surface, and the thermocouple wires hung about 1 cm down over the edge of the propellant surface with small nuts fastened to the wires to keep the thermocouple bead on the propellant surface.
Three approaches for temperature measurements: (A) measures temperature from subsurface to 1 mm above the surface, (B) measures temperature from 1 mm above the surface to the post-flame, and (C) measures surface temperature.
Chapter 4

KINETICS MODELING

The objective for the kinetic modeling is to obtain better gas-phase resolution and quantify the effects of pressure and laser flux on the gas-phase heat feedback during laser-assisted combustion of HMX and AP/HTPB based propellants. Before using the models to obtain the gas-phase heat feedback, efforts were carried out to validate the gas-phase chemical kinetics via comparisons with measured species mole fractions. The models produced species profiles as a function of height above the propellant surface based on some values determined experimentally. These profiles were compared to the species profiles measured by the microprobe/TQMS system and helped validate the current kinetic mechanism for nitramine and AP/HTPB propellants. These kinetic mechanisms were then used through CHEMKIN to obtain the gas-phase heat feedback for both propellant types under various operating conditions.

The first section of the chapter describes the CHEMKIN II code [89,90,91] and the PREMIX subroutine [92], which were used to solve the gas-phase model in the study. The second section presents the physical model and discusses the required inputs to run the model. The kinetic mechanism for modeling HMX and the AP/HTPB based propellants will also be described in the section.
4.1 CHEMKIN II Code and PREMIX Subroutine.

The CHEMKIN II code and PREMIX subroutine, developed by Sandia National Laboratories, are often used to solve the gas-phase model. These two software tools containing a large set of modular subroutines written in Fortran. CHEMKIN II can calculate all the variables needed in modeling gas-phase chemistry based upon user-supplied kinetic mechanisms, thermodynamic properties, and transport properties. The PREMIX subroutine takes the CHEMKIN II output as well as the user-supplied chemical kinetic mechanism and boundary conditions as inputs. Then it can calculate the species, temperature, and velocity profiles by resolving the one-dimensional conservation equations for species, momentum, and energy. The PREMIX program can solve a burner stabilized or freely propagating flame. To use the burner-stabilized approach, the user has the option to use a measured temperature profile as input instead of solving the energy equation. Using the known temperature profile significantly reduces computational time and could also eliminate the uncertainty associated with heat losses in the energy equation. In addition to specifying the temperature profiles, the mass flux fractions at the cold boundary and zero species and gradient at the hot boundary are needed to close the system.
4.2 Physical and Chemical Model

The gas phase was modeled as a one-dimensional, laminar, steady, isobaric, and chemically reacting flow of a premixed gas mixture. The model was solved with the CHEMKIN II software package and the PREMIX subroutine. The flow is governed by the following equations:

\[ M = \rho \cdot u \cdot A \]  
(4.1)

\[ \dot{M} \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx}(kA \frac{dT}{dx}) + A \sum_{i=1}^{N} \rho Y_i V_i c_p \frac{dT}{dx} + A \sum_{i=1}^{N} \omega_i h_i W_i = 0 \]  
(4.2)

\[ \dot{M} \frac{dY_i}{dx} + \frac{d}{dx}(\rho AY_i V_i) - A \omega_i W_i = 0 \]  
(4.3)

\[ \rho = \frac{P W}{RT} \]  
(4.4)

where \( M \) is the mass flow rate, \( \rho \) is density, \( u \) is velocity, \( A \) is the stream tube area, \( T \) is temperature, \( Y \) is mass fraction, \( V \) is diffusion velocity, \( \omega \) is species mole production rate, \( W \) is molecular weight, \( C_p \) is specific heat, and \( k \) is thermal conductivity. The parameter \( x \) denotes the spatial coordinate, the subscript \( i \) refers to the \( i^{th} \) species of which there are \( N \) total species. In the model, the temperature and mole fractions were specified at the cold boundary (at the surface), and zero gradients were imposed at the hot boundary (in the post flame). A similar approach was used by previous studies for modeling the
gas-phase flame chemistry of HMX [84]. The model generated gaseous species profiles as a function of height above the propellant surface. The results could be compared directly to the species profile measured experimentally by TQMS.

To solve the species profiles, the model required as input the mole fractions and the mass flux at the surface as well as the temperature profile in the gas phase. The mass flux was calculated by a mass flux balance at the surface using the burning rate determined by analysis of the video recordings for each experiment. The mole fractions at the surface and the temperature profile in the gas phase were measured experimentally.

### 4.3 HMX Mechanism

The reaction mechanisms used for the current HMX study was based on the two mechanisms mainly developed by Yetter and co-workers [93,94] for RDX. The chemical mechanism in reference 94 is a revised version of the mechanism in reference 93. The previous mechanism of Yetter and co-workers contains 38 species and 178 reactions, while the new mechanism of Yetter and co-workers includes 48 species and 228 reactions. The HMX mechanism was formed by replacing all the reactions associated with RDX, RDXR, and RDXRO in the RDX mechanism with the appropriate molecules for HMX [3]. Due to the lack of information on thermodynamic and transport properties for the HMX molecules, the thermodynamic and transport coefficients for RDX, RDXR and RDXRO were used for HMX, HMXR and HMXRO. The reaction mechanism and species considered in the model are listed in Appendix F.
4.4 AP/HTPB Mechanism

Korobeinichev et al. developed the reaction mechanism used for the gas-phase study of AP/HTPB propellants in this study [95]. Their reaction mechanism consisted of 35 species and 58 elementary reactions. This mechanism was reduced from their previous study that contained 243 reactions and 49 species [96]. In the present study, mathematical difficulties were encountered during the reactions of C$_4$H$_6$ that resulted in C$_4$H$_5$ and C$_4$H$_4$ formation. In order to avoid this problem, a revised version of this mechanism adopted by Jeppson and Beckstead was used [97]. This revised mechanism contained 72 reactions and 35 species. Their mechanism used the GRI mechanism to modify the C$_4$H$_6$ reactions to directly form C$_2$H$_2$ and C$_3$H$_4$ species. The reactions and the species are listed in Appendix G.

4.5 Estimation of the Unsteady Gas-Phase Heat Feedback

The two gas-phase kinetic mechanisms were used to determine the effects of various ambient conditions like pressure and laser flux (via burning rate) on the gas-phase heat feedback. One of the primary driving parameters in oscillatory combustion is the propellant gas-phase heat feedback. Hence these steady-state models were put through iterative loops to obtain unsteady gas-phase heat feedbacks during laser and pressure-driven combustion.
To obtain the gas-phase heat feedback during laser-driven combustion, the laser flux was assumed to affect only the burning rate and the surface temperature. This burning rate was used and the energy equation was solved to obtain the gas-phase heat feedback. The highest, lowest and mean value of the propellant burning rate were used to obtain the gas-phase heat feedback at the highest, lowest and mean value of the laser flux. Clearly these are “pseudo-unsteady” gas-phase heat feedbacks and may not serve as accurate estimates of the unsteady gas-phase heat feedback. However this does serve as a useful first order approximation of the unsteady gas-phase heat feedback.

During pressure-driven combustion, the ambient pressure, burning rates and surface temperatures are changed and the energy equation is solved. The mean and the maximum and minimum values of the gas-phase heat feedback are used to obtain the “pseudo-unsteady” gas-phase heat feedback.

An accurate value for the gas-phase heat feedback can only be obtained through a transient solution. Development of such a model is laborious and hence the “pseudo-unsteady” gas-phase heat feedback has been used to understand the effect of heat feedback on the laser and pressure-driven response functions.
Chapter 5

RESULTS AND DISCUSSION: HMX

This chapter is divided into two sections. Section 1 will focus on the steady-state measurement and analyses of burning rate, temperature and heat release while section 2 covers the unsteady measurements and analyses. Section 5.1 will discuss the measured steady-state sub-surface, surface and gas-phase temperature profiles and the numerically computed surface and gas-phase temperature profiles. The numerically calculated gas-phase temperature profiles were used to determine the steady state and unsteady components of the head feedback from the propellant flame to the propellant surface. The steady-state component of the gas-phase heat feedback was used to calculate the sub-surface heat release via a one-dimensional energy balance, which helps estimate the effect of incident laser-heat flux on condensed-phase heat release and condensed-phase response during laser and pressure-driven combustion.

Section 2 is divided into four sub-sections. Sub-sections 1 and 2 discuss the unsteady laser and pressure-driven thrust response profiles and compares them to modeling and analytical predictions. Sub-section 3 covers the comparison of the laser and pressure-driven response amplitudes, and sub-section 4 attempts to use a transfer function to relate laser and pressure-driven combustion.

5.1 Steady State Analysis
5.1.1 Temperature Measurements

The temperature profiles were derived by piecing together available temperature data from separate experiments. The surface temperature was monitored by attaching a 25 µm platinum/platinum-rhodium thermocouple directly to the regressing surface. During tests, the thermocouple was always attached to the surface due to the weight of small nuts placed on the wires as explained in Chapter 3. Chromel/Alumel, Tungsten/Rhenium and Platinum/Rhodium thermocouples were used in the measurements. All three types of thermocouples were used to estimate the catalytic effect on the temperature measurements near the surface. It is believed that catalytic effects depend on the material thus the different thermocouples will give different temperatures due to different catalytic effects. The surface temperature measurements with different thermocouples were very similar and showed that catalytic effects are negligible during surface temperature measurements.

Figure 5-1 shows the surface and near-surface temperature profiles for HMX at 35, 60 and 90 W/cm² at one atmosphere (101 kPa) in air. The surface temperatures at 35, 60 and 90 W/cm² are 630±10, 635±10 and 645±10 K respectively. At all incident laser fluxes, the gas-phase temperature shows a very gradual rise in the near-surface region. About 1 mm above the propellant surface the temperature is 700 K at incident heat fluxes of 60 and 90 W/cm² while at 35 W/cm², the temperature 1 mm above the propellant surface is 740 K. At 35 W/cm², the temperature profile shows a sharp rise about 1.3 mm
above the propellant surface to a final flame temperature of 2100 K. At 60 and 90 W/cm$^2$, the temperature profiles show a sharp rise about 1.5 and 2 mm above the propellant surface. At all heat fluxes, the temperature rises to a final flame temperature. These profiles are very consistent with the steady-state measurements of Tang [84]. The temperature profiles clearly show that the incident laser flux increases the surface temperature and flame standoff distance above the propellant surface. The temperature profiles are used to estimate the gas-phase heat feedback. These profiles show that the gas-phase heat feedback also decreases with an increase in heat flux.

![Temperature profiles for HMX at 101 kPa and 35, 60 and 90 W/cm$^2$](image_url)

*Figure 5-1* Temperature profiles for HMX at 101 kPa and 35, 60 and 90 W/cm$^2$
Figure 5-2 shows the surface and near-surface temperature profiles for HMX at 35 and 60 W/cm² at two atmospheres (202 kPa) in air. The main focus of these measurements was the near-surface temperature profiles and hence efforts were not made to accurately measure the final flame temperatures. The surface temperatures at 35 and 60 W/cm² are 650±15 and 660±15 K respectively. The temperature profiles once again show a gradual rise near the propellant surface. 1 mm above the propellant surface, the temperatures are 800 and 760 K at heat fluxes of 35 and 60 W/cm² respectively.

The higher pressure decreases the flame stand off distance and the profiles at 35 and 60 W/cm² show a sharp rise to the final flame temperature about 1 and 1.2 mm above the
propellant surface. At one atmosphere, the profiles showed a sharp rise about 1.3 and 1.5 mm above the propellant surface. Hence the higher pressure increases the surface temperature, the gas-phase heat feedback and decreases the flame stand off distance and the length of the primary flame zone.

Figure 5-3 plots the temperature profiles for HMX at 3 atmospheres (303 kPa) in air. The surface temperatures at 35 and 60 W/cm² were 655 and 670 K respectively. At these pressures, the near-surface region of gradual temperature rise is significantly smaller. At 35 W/cm², the primary flame region is of the order of 0.8 mm, while at 60 W/cm², the primary flame region is of the order of 1 mm. Once again there is an absence of a “dark zone” temperature plateau region. At both heat fluxes, the gas-phase heat feedback is significantly higher than at one atmosphere.
Figure 5-3 Temperature profiles for HMX at 303 kPa and 35 and 60 W/cm\(^2\)

Figure 5-4 (a) and (b) are images of the setup used for near-surface temperature measurements for HMX. Figure 5-4 (a) is an image of a steady-state combustion experiment at 1 atmosphere under laser heating at 35 W/cm\(^2\), while figure 5-4 (b) is an image of an experiment performed on HMX at 2 atmospheres with laser heating of 35 W/cm\(^2\). A 75 mm platinum/rhodium thermocouple was used to obtain the near-surface temperature profile during both test cases. The figures clearly show that the flame stand off distance decreased with an increase in pressure.
Figure 5-4 Near-Surface Temperatures for HMX at 1(a) and 2(b) atmospheres.
Table 5-1 lists the burning rates and surface temperatures as a function of heat flux and pressure. Clearly the higher pressures and heat fluxes result in higher burning rates and surface temperatures.

<table>
<thead>
<tr>
<th>Heat fluxes (W/cm²)</th>
<th>101 kPa</th>
<th>202 kPa</th>
<th>303 kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burning rates</td>
<td>0.55</td>
<td>0.74</td>
<td>0.87</td>
</tr>
<tr>
<td>Surface temperature</td>
<td>630</td>
<td>635</td>
<td>645</td>
</tr>
</tbody>
</table>

Table 5-1 Burning rates and Surface temperatures for HMX at various pressures and heat fluxes.

5.1.2 Steady-State Modeling Analysis

The object of this analysis was to use the CHEMKIN code to verify the effects of heat flux on gas-phase temperature profiles and gas-phase heat feedback. Before performing such an analysis, several user inputs from experimental observations were used to validate the code for the gas-phase chemistry of HMX. Initially Yetter and co-workers’ previous chemical mechanism [93] was employed in the gas-phase flame model. The mass flux from the surface was specified based on a burning rate of 0.55 mm/sec at one atmosphere. This burning rate is observed during laser-assisted combustion of HMX at a laser flux of 35 W/cm². The gas composition at the surface and the temperature profile in the gas-phase were used as initial inputs. Previous studies on HMX decomposition reactions had shown that to achieve good agreement between steady-state numerical and experimental data, modifications to the above mechanism
were required [84]. The updated chemical mechanism of Yetter et al. [94] was used along with corrected temperature profiles and an additional sub-routine in the premix code to account for area expansion of the plume. Video recordings of the combustion events suggested that an area expansion of 20% was a reasonable approximation. Some steady-state measurements were performed to verify the accuracy of the chemical mechanism.

Figure 5-5 compares species profiles for HMX versus modeling predictions at one atmosphere at a burning rate of 0.75 mm/sec. This burning rate corresponds to an incident laser flux of 60 W/cm². At 35 W/cm², the final flame was unsteady and would tend to stabilize at larger values of heat flux. Hence the previous studies have measured species profiles at heat fluxes of 100 and 300 W/cm² [84]. Since the unsteady response experiments were carried out at heat fluxes of 35 and 60 W/cm², the species and numerical analyses were performed at a burning rate associated with an incident heat flux of 60 W/cm². The figure shows that the experimental and numerical profiles for NO, CO, HCN and H₂O, with the experimental data presented in closed symbols and the numerical data in open symbols. In the model the NO reduction is still slower than that observed in the experiments. Large emphasis was not placed on this reduction reaction, as the primary focus of this numerical study was to observe the effect of heat flux on near-surface chemistry. Clearly the model does an excellent job in predicting the mole fractions for the species in the near-surface region. With the gas-phase kinetics and predictive abilities of this model now established, the model was used to determine the effect of heat flux on temperature and gas-phase heat feedback.
Figure 5-5 Comparison of experimental data (closed symbols) and model results (open symbols) at a heat flux of 60 W/cm².

Figure 5-6 plots the effect of propellant burning rate on gas-phase temperature profiles at 101 kPa (1 atmosphere). The plots were created using the radiation-corrected temperature profiles along with surface and gas-phase species profiles as input parameters. The effect of heat flux was accounted for via experimental burning rates (mass flux) and surface and gas-phase temperature profiles. The energy equation was solved in the CHEMKIN code and the resulting temperature profiles are displayed in figure 5-6.
The model predicts a final flame temperature of 2800 K. These values are higher than the measured values of 2300-2350 K. As mentioned in previous sections, this study did not place large emphasis on accurate predictions of the final flame temperature. The goal was to observe the effect of burn rate (heat flux) on near-surface temperature profiles. The profiles clearly show that the increase in mass burning rate results in a larger flame stand off distance. The near-surface regions show a gradual temperature rise that is consistent with the experimental measurements. The temperature profiles at both burning rates show a sharp rise to the final flame temperature about 0.85 and 1.5
mm above the propellant surface. The model predicts a shorter primary reaction zone than the experimental data at a burning rate of 0.55 mm/sec but shows very good agreement at the burning rate of 0.75 mm/sec. Similar to the experimental profiles, the model predicts a sharp rise in temperature from the primary reaction zone to the final flame region.

Figure 5-7 plots the effect of burning rate on gas-phase heat feedback. The heat feedback was calculated from the temperature profiles obtained by solving the energy equation in the CHEMKIN code. In order to perform such an analysis, three temperature profiles were selected as standards. The profiles had surface temperatures of 620, 650 and 665 K. Each profile was used as a fixed input parameter and the burning rate was varied from 0.4 to 1.0 mm/sec. This calculation was repeated for the three temperature profiles. This figure clearly shows that for a given surface and gas-phase temperature profile, an increase in burning rate lowers the gas-phase heat feedback. This data should be used very carefully to interpret experimental gas-phase heat feedback because the heat feedback is clearly a function of burning rate and surface temperature while the figure plots the effect of burning rate on heat feedback for only three surface temperatures.
5.1.3 Steady-State Analytical Analysis

The objective of this analysis is to estimate the heat release as a function of the incident laser heat flux in the surface reaction zone. In order to perform a one-dimensional analytical analysis, the condensed phase is assumed to consist of a thin layer where the heat release is significant (surface reaction zone or condensed-phase reaction zone) and a warm-up zone where the heat release is zero [101]. Due to the small
characteristic times for this heat release layer compared to the warm-up zone (preheated zone) quasi-steady assumptions are used.

The conservation of energy can be written as

\[ \rho_c C_c \frac{\partial T}{\partial t} + \dot{m} C_c \frac{\partial T}{\partial x} = k_c \frac{\partial^2 T}{\partial x^2} + \phi(T) \]  \hspace{1cm} (5.1)

where the subscript c stands for the condensed phase, k is the thermal conductivity and \( \dot{m} \) is the mass-flux, \( \dot{m} = \rho_b r_b \) and \( \phi(T) \) is the function of the heat release rate.

Neglecting the time derivative and integrating equation 5.1 gives us the heat release in the reaction layer of the condensed-phase.

\[ C_c \rho_b (T_s - T_o) = \rho_b H + q_r + q_f \]  \hspace{1cm} (5.2)

where \( q_r \) is the radiant heat supply from the gas into the condensed phase and \( q_f \) is the heat feedback that is determined from the temperature gradient at the gas phase side of the propellant surface.

To evaluate the condensed phase reaction zone heat release, the equation can be written as

\[ H = C_c T_s - C_c T_o - \frac{q_f}{\rho_b} - \frac{q_r}{\rho_b} = C_c (T_s - T_o) - \frac{1}{\rho_b} (q_f + q_r) \]  \hspace{1cm} (5.3)

where a positive value of H denotes exothermic heat release.

This heat release is calculated based on experimental values of surface temperature and burning rate. In order to calculate the radiant flux at the propellant surface, the transmissivity of the plume is assumed to be 1. The absorptivity of HMX was assumed to be 0.75 at 10.6 microns. The specific heat was assumed to be 0.35 cal/gmK. At room
temperature the absorptivity of HMX is 0.85 at 10.6 microns [102]. Brewster et al. in the development of their quasi-steady WSB model have assumed the absorptivity of HMX to be 0.5 at 10.6 microns during combustion [42]. They believe that dynamic processes during combustion (bubble formation) reduce the surface absorptivity though the value of 0.5 was adopted to allow the best fit between their experimental and numerical data. Hence an intermediate value of 0.75 was used for surface absorptivity. Table 5-2 lists the sub-surface heat release and burning rates as a function of heat flux and pressure. At a given pressure, the increase in heat flux decreases the heat release in the sub-surface reaction zone. A careful examination of equation 5.3 shows that the increase in heat flux causes a slight increase in the surface temperature and hence increases term 1. The increased heat flux decreases the gas-phase heat feedback term and decreases term 2. The increase in heat flux increases the radiant flux incident on the surface and hence increases term 3. Clearly the table shows that with an increase in heat flux, the increase in term 3 offsets the decrease in term 2 and is larger than the corresponding increase in term 1 and hence the lower condensed-phase heat release at the higher laser fluxes. The heat release values listed in table 5-2 are consistent with the work of Tang [84]. Tang also observed that the measured species profiles at the surface were consistent with the condensed-phase heat release values.
Table 5-2: Effect of pressure and heat flux on heat release in the condensed-phase reaction zone

<table>
<thead>
<tr>
<th></th>
<th>1 atmosphere</th>
<th>2 atmospheres</th>
<th>3 atmospheres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Flux (W/cm²)</td>
<td>35</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>Heat Release (cal/gm)</td>
<td>38±3.5</td>
<td>34±3.5</td>
<td>29±4.5</td>
</tr>
<tr>
<td>Heat feedback (W/cm²)</td>
<td>3</td>
<td>2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

At a given heat flux, an increase in pressure results in higher surface temperatures, higher burning rates and higher temperature gradients at the burning surface. The normalized radiant flux decreases with an increase in pressure. Hence the higher condensed phase heat releases at the higher pressures are due to the increase in surface temperature and corresponding decrease in the normalized radiant flux (normalized by the mass burning rate).

In order to examine this effect theoretically, the decomposition mechanisms for HMX were examined. Melius originally proposed the following decomposition reactions for HMX [103].

\[
\text{HMX} \rightarrow 4(\text{HONO}+\text{HCN}) \quad (5.4)
\]

\[
\text{HMX} \rightarrow 4(\text{CH}_2\text{O}+\text{N}_2\text{O}) \quad (5.5)
\]
The competing reaction branches have been documented in other studies on nitramine models [104]. Brill suggested that these two reactions are global competing reaction branches during the thermal decomposition of condensed-phase HMX. Reaction 5.4 is an endothermic reaction (-38 kcal/mole) while reaction 5.5 is an exothermic reaction (50 kcal/mole). The rate constants for reaction 5.4 and 5.5 are given by equation 5.6 [104].

\[
\begin{align*}
    k_{5.4} &= 10^{16.5} \cdot \exp(-44,100 / RT) \\
    k_{5.5} &= 10^{13.0} \cdot \exp(-34,400 / RT)
\end{align*}
\]  

An increase in surface temperature results in a greater likelihood for reactions to follow the endothermic reaction channel. Table 5-3 calculates the rate constants and surface heat release as a function of surface temperature based on the two reactions described in 5.4 and 5.5. A positive heat release denotes exothermic reactions and the table clearly shows that the increase in surface temperature from 600 to 650 K favors the endothermic reaction pathway and hence results in an endothermic heat release.

The products of these global reactions react in secondary exothermic reactions (NO₂ + CH₂O, HCN + NO₂) that are responsible for producing the heat to sustain pyrolysis. The rate constants for the secondary reactions that take place in the two-phase region might be a function of both temperature and pressure due to the density changes of the reactants in the two-phase region. However, the rate constants and pressure dependence parameters for these secondary reactions are poorly established [104] and hence do not allow for quantitative evaluation of these rate constants at different test pressures. The
entire purpose of this evaluation is to qualitatively compare the effect of heat flux and surface temperature on experimentally and theoretically computed values of the condensed-phase heat release. Clearly the experimental and theoretical values predict the same qualitative trends.

<table>
<thead>
<tr>
<th>Surface Temperature (K)</th>
<th>Rate constant for reaction 5.4 (1/s)</th>
<th>Rate constant for reaction 5.5 (1/s)</th>
<th>Heat release (cal/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>2.7</td>
<td>3.0</td>
<td>27.2</td>
</tr>
<tr>
<td>630</td>
<td>15.9</td>
<td>11.7</td>
<td>-2.8</td>
</tr>
<tr>
<td>650</td>
<td>47</td>
<td>27.2</td>
<td>-20.6</td>
</tr>
<tr>
<td>670</td>
<td>134.3</td>
<td>61.6</td>
<td>-35.5</td>
</tr>
</tbody>
</table>

Table 5-3 Rate constants and heat release as a function of surface temperature.

5.2 Unsteady Combustion

5.2.1 Laser-Driven Combustion

The HMX powder used in the work was obtained from Naval Air Warfare Center-Weapons Division (NAWC) and contained only 0.2\% of RDX as an impurity. The powder was molded into a test sample by using a linear positioner to press it into pellets at a final pressure of 8000 psi. The resulting sample pellet with a diameter of 0.25 " had a density of 1.7 g/cm³.
Since a pellet with a larger diameter produces a higher mass flow rate (thrust), during burning, the thrust to noise ratio increases with the diameter of a pellet. Instead of pressing the powder into pellets with a diameter of 0.25”, they were pressed into cylindrical pellets 0.375” in diameter and 0.25” in height under a consolidation pressure of 4000 psi. This relatively low-pressure value was primarily due to limitations in the pellet pressing facility. Fortunately, the consolidation pressure of 4000 psi produced a pellet density of 1.7 g/cm³. To confine the melt layer and obtain a truly one-dimensional thrust response, the sample was normally placed into a quartz tube during testing. During laser-driven combustion, the CO₂ laser serves as a source of mean and unsteady laser flux. Hence mean and unsteady component of the laser as well as the gas-phase heat feedback are incident on the propellant surface. As discussed in section 5.1.1, the gas-phase heat feedback decreases with an increase in the laser flux. The propellant condensed-phase responds to the summation of the mean and unsteady components of the laser flux and gas-phase heat feedback. Experiments have shown that for the HMX propellants at 1, 2 and 3 atmospheres, the gas-phase heat feedback is smaller in magnitude than the laser flux and out of phase with the laser flux. Hence the laser-driven response experiments are primarily a condensed-phase response to the unsteady laser flux.

5.2.1.1 Laser-Driven Combustion at One Atmosphere

Tests were performed at atmospheric pressure in air at heat fluxes of 35±15, 60±15 and 90±15 W/cm² and driving frequencies ranging from 3.9 to 250 Hz. Use of air,
instead of argon, is due to the fact that the test chamber is open to the atmosphere. All tests were done using a heat flux sweep with discrete increments of frequency. The time interval for each frequency often covered several cycles. To make sure that “steady state” oscillating conditions were reached; the first cycle for a given frequency normally was not considered during data analysis. The specific frequencies for the tests were chosen so that an integer multiple of a period exactly covered $2^n$ data points. The thrust signals beyond 250 Hz were not considered due to an unacceptable noise to signal ratio.

A previous study reported the thrust, species, and light emission response data under sinusoidal laser heating [84], and was the foundation for the laser-driven response measurements obtained in the current study. There was considerable scatter in the thrust response amplitude and phase data obtained under the previous study. One of the objectives behind repeated measurements of the thrust-response for HMX was to verify and establish the amplitude and phase response behavior as a function of laser flux.

During thrust response tests, the first few cycles after ignition showed the presence of noise at a frequency of 200 Hz. This noise lasted only a few cycles and decayed with time. This portion of data was always ignored in data reduction. It was found that the frequency of the noise depended on the open area of the test chamber and was independent of the sample material. This noise was a result of the test chamber acting as a Helmholtz resonator.

Figure 5-8 shows the thrust amplitude and phase responses at heat fluxes of 35±15 and 60±15, and 90±15 W/cm$^2$. The normalized thrust amplitude is defined as $\Delta \tau/\Delta q$, where $\Delta \tau$ is the thrust amplitude in mNewton, and $\Delta q$ is the heat flux amplitude in Watts.
The average burning rates at incident laser heat fluxes of 35, 60 and 90 W/cm$^2$ were 0.55, 0.74 and 0.87 mm/s respectively.

For all three incident heat fluxes, the thrust amplitude is small at low frequency, increases to a peak and then decreases with an increase in frequency. This is consistent with the classical modeling results obtained under the QSHOD framework. Figure 5-8 (a) shows that an increase in the mean heat flux decreases the response amplitude and appears to shift the resonant peak to a higher dimensional frequency. This trend has also been observed in the work of Zarko et al [55]. At a mean heat flux of 35 W/cm$^2$, the maximum thrust amplitude was 0.015 mN/W at 12 Hz. The maximum thrust response of 0.0135 mN/W was measured at 16 Hz with a mean laser heat flux of 60 W/cm$^2$. At 90 W/cm$^2$, the maximum amplitude of 0.007 mN/W was observed at 32 Hz. A 95% confidence interval based on multiple experiments performed at each condition was used to calculate the random error. This scatter is displayed on the figures as error bars.

Figure 5-8 (b) shows the relative phase signal as a function of frequency and heat flux. The phase signal shows a lead at low frequency, which decreases monotonically to a lag as frequency increases. For an incident heat flux of 35 W/cm$^2$, the phase signal shows a lead of 21 degrees at 4 Hz, zero at 12 Hz, and a lag of 46 degrees at 250 Hz. The maximum response amplitude is measured at 12 Hz and the relative phase at this frequency is zero. The phase signal at 60 W/cm$^2$ shows a lead of 44 degrees at 4 Hz and decreases monotonically to a lag of 45 degrees at 250 Hz. At 90 W/cm$^2$, the phase shows a lead of 48 degrees at 4 Hz, and decreases monotonically to a lag of 43 degrees at 250 Hz.
(a)  
Figure 5-8 HMX thrust amplitude and phase responses at heat fluxes of 35±15, 60±15 and 90±15 W/cm²
Though sinusoidal laser heating was imposed on the propellant, the propellant surface was not heated by a purely sinusoidal heat flux due to the fact that the heat feedback from the gas phase was not in phase with external radiation. If the interaction between the heat feedback and burning rate was the point of interest, the amplitude for external radiation should be as small as possible such that the heat feedback was the dominant heat flux on the surface. At a laser flux of 35 W/cm², the gas-phase heat feedback is about 3 W/cm² and section 5.1.1 of this chapter clearly shows that the heat feedback decreases with an increase in heat flux. Unfortunately, it was very difficult to use a heat flux amplitude of less than ±15 W/cm² due to the poor signal to noise ratio.

Figure 5-9 shows the thrust response at a frequency of 3.9 Hz and a heat flux of 35±15 W/cm². The thrust response signal is asymmetric and rises much quicker than it drops. This non-sinusoidal shape of the response signal was also reported by Zarko et al. [55]. The non-sinusoidal signals generally occurred at a frequency below 8 Hz. The thrust data at different heat fluxes showed that increasing the mean heat flux and decreasing the heat flux amplitude generated signals that were closer to sinusoidal. The amplitude and phase for the non-sinusoidal signals were difficult to determine. Thus, the uncertainties for 35±15 at a frequency of 3.9 Hz were relatively large. The signals suggest that the assumption of a sinusoidal response used in analytical models may not be correct at these test conditions.
In this study, the heat feedback is much smaller than the laser power, and hence the experimental data for laser-driven combustion response only indicates the condensed-phase response to the laser flux. It is believed that the peak in the amplitude response curve (figure 5-8) is related to the condensed phase thermal relaxation. The thermal relaxation time is defined by equation 5.7.

\[ t_c = \frac{\alpha}{r_b} \]  \hspace{1cm} (5.7)

where \( r_b \) is the steady state propellant burning rate, and \( \alpha \) is the thermal diffusivity.

Figure 5-9 Typical thrust response for HMX at a frequency of 4 Hz.
An increase in the mean heat flux increases the burning rate and decreases the thermal relaxation time. Hence the amplitude peak shifts to a higher dimensional frequency. This is clearly visible in the heat flux amplitude response for HMX.

In order to compare propellant response functions at different test conditions, most research groups used a non-dimensional frequency, $\Omega$, instead of frequency, Hz, in their analytical and modeling studies. This non-dimensional frequency relates the driving frequency (Hz) to the characteristic relaxation time of the thermal wave in the solid phase. The non-dimensional frequency is defined as:

$$\Omega = \frac{\alpha \cdot \omega}{r_b^2} \quad (5.8)$$

where $\alpha$ is the thermal diffusivity of the propellant and $\omega$ is the oscillation frequency (rad/s).

Figure 5-10 shows the amplitude and phase responses at different heat fluxes as a function of $\Omega$. To obtain $\Omega$, the $\alpha$ for HMX is assumed to be 0.0008 cm$^2$/s [101]. It is evident that the resonant peaks at different heat fluxes occurred at about the same non-dimensional frequency of 16-20. Based on non-dimensional frequency, the results agreed with most analytical modeling and T-burner experimental results for homogenous propellants [13,50,51,54].
Figure 5-10  Thrust amplitude and phase versus $\Omega$ at 35±15, 60±15, and 90±15W/cm$^2$. 
It is also important to convert the dimensional laser-driven response amplitudes into non-dimensional format. This is essential to facilitate comparisons between experimental data and the theoretical and numerical studies present in the literature. The non-dimensional response can be obtained by one of two methods:

a) Make assumptions about the flame shape, measure the flame temperature and estimate the average molecular weight of the gas-phase species.

b) Perturb the thrust equation (5.10) to experimentally obtain all required parameters.

This study focused on the second method to obtain the thrust response and the approach is described in the next few paragraphs.

The heat flux response, \( R_q \), is defined as equation (5.9)

\[
R_q = \frac{\Delta m / \overline{m}}{\Delta q / \overline{q}}
\]  

(5.9)

where \( \overline{q} \) is the mean heat flux, \( \Delta q \) is the heat flux amplitude \( \overline{m} \) is the mean burning rate, and \( \Delta m \) is the burning rate amplitude. The relation between burning rate and thrust can be derived by the steady state momentum equation [33]. The thrust can be displayed as equation (5.10)

\[
\tau = \overline{m}^2 \left( \frac{RT_f}{PM} \right)
\]  

(5.10)

where \( \tau \) is the mean thrust, \( R \) is the universal gas constant, \( P \) is the ambient pressure, \( T_f \) is the flame temperature, and \( M \) is the average molecular weight. By perturbing equation (5.11), the oscillating thrust can be given as

\[
\Delta \tau = 2m\Delta m \left( \frac{RT_f}{PM} \right)
\]  

(5.11)
From equations (5.10) and (5.11), the oscillating burning rate can be given as equation (5.12).

\[ \Delta m = \Delta \tau \frac{\overline{m}}{2\overline{\tau}} \]  

(5.12)

By substituting equation (5.12) into equation (5.9), the heat flux response can be displayed as equation (5.13)

\[ R_q = \frac{\Delta \overline{m} / \overline{m}}{\Delta q / \overline{q}} = \frac{\Delta \tau \overline{m} \overline{q}}{\Delta q \overline{2\tau \overline{m}}} \]  

(5.13)

\[ \Delta \tau / \Delta q \] and \[ \overline{q} / \overline{m} \] could be obtained through the oscillating heat flux tests, but \[ \overline{m} / \overline{\tau} \] was still an unknown. To obtain \[ \overline{m} / \overline{\tau} \], a series of square wave heat fluxes were imposed on the HMX pellet. When steady state burning was reached, the laser was cut off so that the burning suddenly stopped. Thus, the steady state burning rate and the thrust at the burning rate could be obtained experimentally. Figure 5-11 plots \[ \overline{m} / \overline{\tau} \] as a function of burning rate. The corresponding values of \[ \overline{m} / \overline{\tau} \] are used to convert the measured dimensional response to a more conventional non-dimensional response. The ordinate is a ratio of the burn rate in mm/sec to thrust in Newtons. Thus, the heat flux response \( R_q \) can be obtained without making assumptions about the flame shape and the gas temperature to molecular weight ratio.
Figure 5-11 Relation between burning rate and burning rate to thrust ratio

Figure 5-12 shows experimentally obtained $R_q$ as a function of frequency at laser heat fluxes of 35, 60 and 90 W/cm². The solid symbols are quasi-steady modeling data obtained from Erikson et al. at BYU [26]. The non-dimensional $R_q$ shows a small decrease from 1.25 to 1.18 for the maximum amplitude during experiments at heat fluxes of 35 and 60 W/cm². The modeling results predict a small increase in $R_q$ from 0.35 to 0.4 with an increase in laser heat flux from 35 to 60 W/cm². Figure 5-8 had shown that an increase in the heat flux decreased the dimensional burn rate response. Equation 5.13 shows that the non-dimensional $R_q$ is dependent on the ratio of three parameters. The decrease in dimensional response ($\Delta \tau / \Delta q$) from 35 to 60 W/cm², was partially offset by a corresponding increase in the $\tau / \tau_c$ and $\varphi / \tau$ ratios. Erikson predicts an increase in the
non-dimensional amplitude response that is within the experimental uncertainties of this study. Thus, the present study cannot confirm this predicted increase. Erikson believes that the lower values for the response amplitudes obtained by the modeling efforts may be due to inaccurate $\sigma_p$ data and chemistry in the condensed phase and near-surface gas phase regions for HMX [3]. A further increase in the heat flux from 60 to 90 W/cm$^2$ decreased the experimental maximum response amplitude to 0.84. This decrease in not predicted in the modeling efforts, but is observed by others [39,52,55].

Figure 5-12 Experimental and numerical laser-driven response at 35, 60 and 90 W/cm$^2$
To evaluate the reasons for the small decrease in response amplitude with an increase in laser flux from 35 to 60 W/cm², the steady-state temperature profiles and energy balance are evaluated. Steady state temperature and energy analyses suggest that there is a small change in surface temperature (630 and 635) and condensed phase heat release (38 and 34 cal/gm) at incident heat fluxes of 35 and 60 W/cm². As documented earlier the major effects of the increase in the laser flux from 35 to 60 W/cm² are the higher burning rate, and the lower gas-phase heat feedback. The steady-state component of the gas-phase heat feedback decreases from 3 to 2 W/cm² with the increase in laser flux. The unsteady components of the gas-phase heat feedback were estimated by running Chemkin and are best illustrated through the following steps:

a) Use table 5-1 to relate the steady-state burning rate data and mean laser flux.

b) Obtain steady-state burning rate values for the maximum and minimum values of the laser flux. (r_b at 20 and 50 W/cm² for a laser flux of 35±15 W/cm²).

c) Solve the energy equation through Chemkin using these burning rates at 1 atmosphere and obtain temperature profiles and gas-phase heat feedbacks.

Table 5-4 lists the steady and unsteady components of the laser flux at 35, 60 and 90W/cm². The absorptivity of the laser flux at the surface is assumed to be 0.75. Hence the mean surface laser fluxes are 26.3, 45 and 67.5 W/cm². The gas-phase heat feedbacks are 3±0.6, 2±0.45 and 0.7±0.5 W/cm² at the three laser fluxes. Since the unsteady components of the heat feedback are out of phase with the laser flux, an increase in the unsteady component of the heat feedback, decreases the unsteady total flux incident on the propellant surface. The unsteady component of the laser flux is much larger than the
unsteady component of the heat feedback and hence masks the change in heat feedback with laser flux resulting in the nearly constant response amplitudes.

<table>
<thead>
<tr>
<th>Unsteady laser flux (W/cm²)</th>
<th>Surface Laser flux (W/cm²)</th>
<th>heat feedback (W/cm²)</th>
<th>Total heat flux (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35±15</td>
<td>26.3±11.3</td>
<td>3±0.6</td>
<td>29.3±10.7</td>
</tr>
<tr>
<td>60±15</td>
<td>45±11.3</td>
<td>2±0.45</td>
<td>47±10.85</td>
</tr>
<tr>
<td>90±15</td>
<td>67.5±11.3</td>
<td>0.7±0.5</td>
<td>68.2±10.8</td>
</tr>
</tbody>
</table>

Table 5-4 Total heat flux as a function of unsteady laser-flux during laser-driven combustion.

The small changes in surface temperature and heat release at the two laser fluxes suggests similar properties and behavior of the condensed phase. With the laser amplitude overwhelming the effect of gas-phase heat feedback, one would expect a small change in response amplitude and phase between these two test conditions.

At the incident heat flux of 90 W/cm², the unsteady net flux incident on the propellant surface is very similar to the tests at 35 and 60 W/cm². However the response amplitudes are much lower at 90 W/cm². This is probably due to the higher surface temperature (645 K) and the lower heat release in the condensed-phase reaction zone (23 cal/gm). The Ph.D. thesis of Tang showed that HMX at 30 W/cm² underwent self-oscillatory combustion at 1 atmosphere [84]. This self-oscillatory combustion was believed to be due to the exothermic and endothermic decomposition mechanisms having similar reaction rates. This resulted in a coupling between the two mechanisms and
hence self-oscillatory behavior. The increase in laser flux increased the surface temperature and resulted in greater probability for the reactions to follow the endothermic pathway (equation 5.4). Hence the probability for self-oscillatory behavior decreased and resulted in the lower response amplitudes. Section 5.1.3 showed that an increase in the laser flux results in lower amounts of exothermic heat release in the condensed-phase and hence for HMX, a decrease in the condensed-phase exothermicity resulted in lower response amplitudes.

5.2.1.2 Laser-Driven Combustion at Higher Pressures

Laser-driven combustion of HMX was carried out at incident heat fluxes of 35 and 60 W/cm² in air at initial pressures of 2 and 3 atmospheres. In order to compare the data at higher pressures, to the laser-driven data at one atmosphere, compressed air was used as the ambient gas. The laser-driven combustion experiments were performed in the chamber that was originally designed for pressure-driven combustion. At test pressures above three atmospheres, the potassium chloride lens at the top of the chamber would rupture and result in depressurization. Hence the experiments were limited to an upper pressure limit of three atmospheres. The burning rates at the initial pressures of two and three atmospheres were 0.8 and 1.05 mm/s at a laser flux of 35 W/cm², and 1 and 1.25 mm/s at a laser flux of 60 W/cm².

Figure 5-13 plots the thrust response amplitude for HMX during laser-driven combustion in air at 2 atmospheres with laser heat fluxes of 35 and 60 W/cm². The
profiles at both heat fluxes show low amplitudes at low frequency followed by a sharp peak and then decrease in amplitude at driving frequencies above this peak. The amplitude trends are very similar to those observed during experiments at 1 atmosphere. The maximum thrust response amplitude at 35 and 60 W/cm$^2$ are 0.02 mN/W at 16 Hz, and 0.017 mN/W at 24 Hz. The maximum thrust response amplitudes decrease with an increase in heat flux and occur at higher dimensional frequencies. At 4 Hz, the thrust response amplitudes are 0.016 and 0.014 mN/W at laser fluxes of 35 and 60 W/cm$^2$ respectively. The thrust response amplitudes decrease to 0.008 and 0.01 mN/W at 250 Hz.

![Figure 5-13 Thrust response amplitude for HMX at 202 kPa and laser fluxes of 35 and 60 W/cm$^2$ in compressed air.](image)

Figure 5-13 Thrust response amplitude for HMX at 202 kPa and laser fluxes of 35 and 60 W/cm$^2$ in compressed air.
Figure 5-14 plots the thrust response amplitude for HMX at 3 atmospheres and laser fluxes of 35 and 60 W/cm$^2$ with compressed air as the ambient gas. The thrust response amplitudes again display a response profile that shows small response amplitude at low frequency, followed by a sharp peak at resonant frequency and then a decrease in amplitude with a further increase in frequency. At 35 W/cm$^2$, the thrust response amplitude increases from 0.018 mN/W at 4 Hz, to its maximum amplitude of 0.022 mN/W at 24 Hz and then decreases to 0.013 mN/W at 250 Hz. The thrust response amplitude at 60 W/cm$^2$, increases from 0.015 mN/W at 4 Hz, to 0.02 mN/W at 32 Hz and then decreases to 0.009 mN/W at 250 Hz. The dimensional response amplitude at 3 atmospheres is larger than the response amplitudes at 2 atmospheres that in turn are larger than the amplitudes at 1 atmosphere.
Figure 5-14 Thrust response amplitude for HMX at 303 kPa at laser fluxes of 35 and 60 W/cm² in compressed air.

Figure 5-15 shows the non-dimensional thrust response amplitude as a function of frequency at 101, 202 and 303 kPa for a laser flux of 35 W/cm². The figure shows that the response amplitude profiles are very similar at the three test pressures. The increase in pressure results in a decrease in the maximum response amplitude from 1.24 at 101 kPa (1 atmosphere) to 1.15 at 303 kPa (3 atmospheres). There is a pronounced shift in the resonant frequency of the condensed phase response amplitude to the increase in pressure. The resonant frequency shifts from 12 Hz at 101 kPa (1 atmosphere), to 24 Hz at 303 kPa (3 atmospheres).
Figure 5-15 Response amplitudes during laser-driven combustion at a mean flux of 35 W/cm² and pressures of 101, 202 and 303kPa in air.

Figure 5-16 Response amplitudes during laser-driven combustion at a mean flux of 60 W/cm² and pressures of 101, 202 and 303kPa in air.
Figure 5-16 plots the effect of pressure on the response amplitude during laser-driven combustion at a mean flux of 60 W/cm². The effect of pressure is very similar to the laser-driven experiments at 35 W/cm². The response amplitude decreases slightly from 1.2 at 1 atmosphere, to 1.05 at 2 atmospheres. The location of the response amplitude shifts to a higher dimensional frequency at the higher pressures. This is a characteristic of the condensed-phase thermal relaxation.

To understand the effect of pressure on the response amplitudes at both laser fluxes, the mean and unsteady components of the gas-phase heat feedback are estimated.

Tables 5-1 and 5-2 clearly showed that the increase in pressure results in an increase in the surface temperature and surface heat release and figures 5-1, 5-2 and 5-3 showed that the increase in pressure decreases the flame standoff distance and increases the gas-phase heat feedback. At a given pressure, the gas-phase heat feedback is out of phase with the laser flux. Hence an increase in the laser flux, decreases the gas-phase heat feedback. At a laser flux of 35 W/cm² and a pressure of 101 kPa, the gas-phase heat feedback is 3 W/cm² while at 303 kPa, the gas-phase heat feedback is 8 W/cm². With the increase in pressure, there is a decrease in the net flux that is incident on the surface. The net flux is defined as the difference between the laser flux and the gas-phase heat feedback.

Table 5-5 lists the mean and unsteady components of the laser fluxes and heat feedbacks and the net heat flux at the three pressures. The table shows that the increase in pressure results in higher values for the unsteady component of the gas-phase heat feedback. Hence the total unsteady flux incident on the propellant surface decreases.
Since the propellant condensed-phase responds to these dynamic changes, a decrease in the total unsteady flux results in the lower response amplitudes. It should be noted that the unsteady laser fluxes are still significantly larger than the unsteady gas-phase heat feedback and hence tend to mask the effect of the changes in the gas-phase heat feedback resulting in only small changes in the response amplitudes.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Surface Laser flux (W/cm²)</th>
<th>heat feedback (W/cm²)</th>
<th>Total heat flux (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 atmosphere</td>
<td>26.3±11.3</td>
<td>3±0.6</td>
<td>29.3±10.7</td>
</tr>
<tr>
<td></td>
<td>45±11.3</td>
<td>2±0.45</td>
<td>47±10.85</td>
</tr>
<tr>
<td>2 atmospheres</td>
<td>26.3±11.3</td>
<td>6.3±1.8</td>
<td>32.6±9.5</td>
</tr>
<tr>
<td></td>
<td>45±11.3</td>
<td>4±1.6</td>
<td>49±9.7</td>
</tr>
<tr>
<td>3 atmospheres</td>
<td>26.3±11.3</td>
<td>8.2±2.7</td>
<td>34.5±8.6</td>
</tr>
<tr>
<td></td>
<td>45±11.3</td>
<td>6±2.3</td>
<td>55±9</td>
</tr>
</tbody>
</table>

Table 5-5 Heat flux as a function of pressure during laser-driven combustion

### 5.2.2 Pressure-Driven Combustion

The HMX powder obtained from NAWC was once again pressed into cylindrical pellets 0.375” in diameter and 0.25” in height. The propellant samples were placed in a quartz vial during response measurements to confine the melt layer and obtain a nearly
one-dimensional thrust response. Tests were performed at an initial pressure of one atmosphere with air as the ambient gas and at mean incident laser heat fluxes of 35 and 60 W/cm². The driving frequencies ranged from 4 to 96 Hz. Unlike the laser-driven tests, each test was performed at only one driving frequency. The tests were limited to 96 Hz due to excessive vibrations from the airplane engines and the test rig. This vibration severely affected the signal to noise ratio and did not allow collection of any meaningful data above this frequency. Due to the small chamber volume, the ambient pressure rose from 1 to 1.5 atmospheres during pressure-driven combustion. Hence the response data were collected at 1.5 atmospheres.

5.2.2.1 Pressure-driven combustion at one atmosphere

Figure 5-17 shows the thrust amplitude and phase response during pressure-driven combustion of HMX with mean heat fluxes of 35 and 60 W/cm². The normalized thrust amplitude is defined as \( \Delta \tau / \Delta p \), where \( \Delta \tau \) is the thrust amplitude in Newtons, and \( \Delta p \) is the pressure amplitude in atmospheres. The average burning rates at incident laser heat fluxes of 35 and 60 W/cm², were 0.60 and 0.79 mm/s respectively. Unlike the laser-driven experiments, pressure-driven response measurements are primarily a condensed-phase response to the unsteady gas-phase heat feedback. The laser serves as a heat source to sustain combustion and does not play any direct role in the dynamic processes that take place during pressure-driven combustion.
Figure 5-17 Thrust Response for HMX during pressure-driven combustion at 101 kPa.
For both incident heat fluxes, the thrust amplitude is small at low frequency, increases to a peak and then decreases with an increase in frequency. These results are consistent with the results obtained under the QSHOD framework. Figure 5-17(a) shows that an increase in the mean heat flux decreases the response amplitude and appears to shift the resonant peak to a higher dimensional frequency. At 35 W/cm$^2$ the maximum amplitude is 8.7 E$^{-4}$ N/atm, while at 60 W/cm$^2$, the maximum amplitude is 7.8 E-$4$ N/atm. The maximum amplitude is observed at 12 Hz for an incident heat flux of 35 W/cm$^2$, while the maximum amplitude is observed at 16 Hz, for an incident heat flux of 60 W/cm$^2$. The shift in resonant frequency with the heat flux is due to the thermal relaxation effect and helps verify the postulate that the first peak (in this study the only peak) is a result of the condensed phase thermal relaxation.

Figure 5-17 (b) shows the phase response to pressure-driven combustion. At both heat fluxes, the phase shows a lead of about 25 degrees at 4 Hz, and this decreases monotonically to a lag of about 30 degrees at 96 Hz. At a heat flux of 35 W/cm$^2$, the phase is almost zero at 12 Hz, and at 60 W/cm$^2$, the phase is almost zero at 16 Hz. The relative phase should be zero at resonant frequency (maximum thrust amplitude). This is observed in these experiments and shows consistency in the amplitude and phase measurements during pressure-driven combustion.

To facilitate comparison to the theoretical and modeling studies, the response amplitude data was converted to a non-dimensional format. The technique used to obtain
the non-dimensional laser-driven thrust response was used to obtain the non-dimensional pressure-driven thrust response.

The pressure-coupled response is defined by equation 5.14

\[ R_p = \frac{\frac{\Delta m}{\bar{m}}}{\frac{\Delta p}{\bar{p}}} \]  \hspace{1cm} (5.14)

where \( \bar{p} \) is the mean pressure, \( \Delta p \) is the pressure amplitude, \( \bar{m} \) is the mean burning rate, and \( \Delta m \) is the burning rate amplitude. The thrust can be displayed as equation (5.15)

\[ \bar{\tau} = \bar{m}^2 \left( \frac{RT_f}{PM} \right) \] \hspace{1cm} (5.15)

This equation is perturbed and manipulated to obtain the pressure-coupled response shown in equation 5.16.

\[ R_p = \frac{\frac{\Delta m}{\bar{m}}}{\frac{\Delta p}{\bar{p}}} = \frac{\Delta \tau}{\Delta p} \cdot \frac{\bar{m}}{2 \cdot \bar{\tau} \cdot \bar{m}} \] \hspace{1cm} (5.16)

The non-dimensional frequency is shown in equation 5.17

\[ \Omega = \frac{\alpha \cdot \omega}{r_b^2} \] \hspace{1cm} (5.17)

Figure 5-18 plots the non-dimensional response amplitude for HMX plotted against the non-dimensional frequency. The solid symbols are modeling data obtained from Erikson at BYU [3]. The maximum thrust response amplitude shows a clear decrease with an increase in heat flux for both the experimental as well as the modeling results. At 35 W/cm², the maximum amplitude is 1.6, while at 60 W/cm², the maximum amplitude is
1.4. The maximum amplitude in the models decreases from 0.96 to 0.8 with an increase in heat flux. The experimental results appear to be consistent with the modeling efforts in trends for the maximum amplitude response. Erikson believes that the lower response amplitudes predicted by the model are believed to be due to inaccuracies in the $\sigma_p$ data, and inadequacies in the decomposition reactions for HMX [3].

To understand the effects of laser flux on the pressure-driven response amplitudes, the surface temperature, energy balance and analytical modeling of pressure-coupled response are evaluated. Surface temperatures during steady-state combustion have been measured to be 630 and 635°C at 35 and 60 W/cm$^2$ respectively. The increase in surface temperature with laser flux could result in a greater amount of decomposition reactions in the condensed-phase. In 1967, Culick developed a model including condensed phase decomposition and found that an increase in the exothermic heat release in the sub-surface would decrease the peak of the response function [6]. However in section 5.1.3, the experimental results of this study were used to show that the surface heat release decreases with an increase in laser flux. Theoretically this is believed to be due to the dominance of the global endothermic decomposition pathway at higher surface temperatures [Table 5-3].

In order to better understand the effect of laser flux on pressure-driven response amplitudes, the mean and unsteady gas-phase heat feedbacks are evaluated. The unsteady component of the gas-phase heat feedback is computed by using an algorithm similar to the laser-driven combustion experiments. The experimentally determined burning rate pressure exponent is used to calculate the burning rate at 1.58 and 1.43 atm
(Since the pressure-driven response is measured at 1.5 atm). The energy equation is then solved for these burning rates and pressures through Chemkin to obtain the steady and unsteady gas-phase heat feedback. Since the pressure-driven response measurements are believed to be condensed-phase responses to these unsteady gas-phase heat feedbacks, a decrease in gas-phase heat feedback with an increase in laser flux would result in a lower response amplitude. This modeling effort through Chemkin to obtain a “pseudo-unsteady” gas-phase heat feedback could validate this postulate.

Table 5-6 shows that the increase in mean laser flux results in a lower unsteady component of the gas-phase heat feedback. Since the propellant condensed-phase responds to this unsteady heat feedback, a lower heat flux results in a lower response amplitude. Hence the increase in laser flux produces the lower response amplitudes.

<table>
<thead>
<tr>
<th>Laser flux (W/cm²)</th>
<th>Surface Laser flux (W/cm²)</th>
<th>Heat feedback (W/cm²)</th>
<th>Total heat flux (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>26.3</td>
<td>4±1.3</td>
<td>30.4±1.3</td>
</tr>
<tr>
<td>60</td>
<td>45</td>
<td>2.5±0.95</td>
<td>47.5±0.95</td>
</tr>
</tbody>
</table>

Table 5-6 Total heat fluxes as a function of the mean laser-fluxes during pressure-driven combustion.
The pressure-coupled response values at 35 and 60 W/cm² were used to obtain FM parameters (equation 2.1, 2.6-2.9). This was an effort to check the experimental FM parameters against the expected values. The objective was to perform an “in the ballpark” analysis. Table 5-7 shows the experimentally computed A, B, n and nₛ parameters for HMX during pressure-driven combustion with incident heat fluxes of 35 and 60 W/cm². Two test cases were tried

Case 1) nₛ was set to zero and A, B and n were obtained.

Case 2) No constraints were set.
Table 5-7 Experimental values for A, B, n and $n_s$ from pressure-driven combustion of HMX.

The assumption that $n_s$ is zero is based on the theory that there exists a unique relationship between the propellant burning rate and its surface temperature [15]. Beckstead suggests that constraining the $n_s$ value to zero is a valid assumption for HMX [15]. The obtained values are of the same order of magnitude and appear to be quite reasonable. The standard errors that are listed in the table are based on the standard deviation.

The A parameter is a function of the initial and surface temperatures, and the activation energy while the B parameter is a function of the initial and surface temperatures and the temperature sensitivity. Hence the steady-state temperature measurements of the surface were used to determine the effect of heat flux on the activation energy and temperature sensitivity.

Table 5-1 and figure 5-1 show the surface and near-surface temperature profiles for HMX at 35 and 60 W/cm². At an incident laser heat flux of 60 W/cm², the surface
temperature of 635 K and the A value of 13.8 resulted in an activation energy of 35 kcal/mol. The activation energy for HMX is believed to be around 42-44 kcal/mol [15]. The B value of 1.24 is well within the expected range of 0.4-2.0 and the resulting $\sigma_p$ value of 0.0023 K$^{-1}$ is reasonable for HMX. The B and $\sigma_p$ parameters obtained from the measured pressure-driven response functions for HMX are quite realistic while the A parameter is slightly higher than the expected value. Culick observed that there could be variations in surface roughness, inhomogeneity and chemistry between the steady state and transient measurements, which could cause variations in the values for activation energy [6]. This would suggest that large emphasis should not be placed on the deviation of the A values from the expected range of 9.3-9.5.

The A and B values at the laser flux of 35 W/cm$^2$ are 27 and 0.92, respectively. The A value shows poor agreement with the expected values while the B value shows good agreement. The surface temperature of 630 K resulted in an activation energy of 63 kcal/mol. This activation energy is higher than the expected values of 42-44 kcal/mole, while the $\sigma_p$ value of 0.0033 K$^{-1}$ is reasonable.

Since the A value is a function of the surface temperature and activation energy, it should show little variation with heat flux as the surface temperatures are nearly constant. At the laser fluxes of 35 and 60 W/cm$^2$, the A values are 13.8 and 27, respectively. This variation of the A value with laser flux cannot be explained at this time. Since this value was obtained by performing a least squares fit of the response curves, the variation in A values is probably due to experimental uncertainties.
The activation energies obtained under case 2, where \( n_s \neq 0 \), at laser fluxes of 35 and 60 W/cm\(^2\) were 110 and 90 Kcal/mol. Clearly these values are much higher than the expected values, while the obtained \( n_s \) parameters are large negative values and hence unrealistic.

Hence table 5-7 is best used as a tool for comparison between the values of Beckstead et al., and case 1 where the \( n_s \) parameter is set to zero.

5.2.2.2 **Pressure-driven combustion at higher pressure**

Figure 5-19 shows the non-dimensional thrust amplitude and phase response during pressure-driven combustion of HMX at an initial pressure of 202 kPa with mean laser fluxes of 35 and 60 W/cm\(^2\). The burning rates were 0.85 and 1.05 mm/s at mean laser fluxes of 35 and 60 W/cm\(^2\) respectively. Due to the higher initial pressure, it was difficult to prevent leakage past the liners of the airplane engines. Hence the chamber was filled with compressed air just before the experiment to a pressure slightly above 2 atmospheres. During combustion, the solid propellant produced a large amount of gaseous products and resulted in a pressure rise to \(~ 225\) kPa.
Figure 5-19 Non Dimensional Pressure Driven Response for HMX at 202 kPa.
The peak response amplitudes are 1.8 and 1.7 at laser fluxes of 35 and 60 W/cm². The peak response amplitudes at laser fluxes of 35 and 60 W/cm² were detected at driving frequencies of 16 and 24 Hz, while at 101 kPa the peak response amplitudes were observed at driving frequencies of 12 and 16 Hz. Clearly the increase in pressure resulted in an increase in the resonance frequency. The maximum response amplitude is believed to be a function of the condensed phase thermal relaxation. The condensed-phase thermal relaxation time is dependent on the propellant burning rate and decreases with an increase in burning rate. Hence the frequency associated with this condensed-phase relaxation increases with an increase in burning rate. The shift of the maximum response amplitude to a higher dimensional frequency verifies the postulate that the response amplitude is related to the condensed-phase thermal relaxation. This effect will be evident in later figures that plot and compare the effects of pressure on the response amplitude versus non-dimensional frequency.

Figure 5-19(b) shows the relative phase between the thrust and the driving frequency at laser fluxes of 35 and 60 W/cm². The phases lead at low frequency and then decrease steadily to zero at the frequency of maximum response amplitude and then lag at high frequency. The phase and amplitude measurements are qualitatively consistent with QSHOD predictions.

Figure 5-20 plots the pressure-driven response for HMX at 303 kPa at 35 and 60 W/cm². At 35 and 60 W/cm², the peak response amplitudes of 2.0 and 1.8 are observed at driving frequencies of 24 and 32 Hz. Again the increase in the ambient pressure results in larger response amplitudes and also shifts the peak to a higher frequency.
Figure 5-20 Non Dimensional Pressure Driven Response for HMX at 303 kPa.
Figures 5-18, 5-19 and 5-20 show that the pressure-driven response amplitudes increase with an increase in pressure from 1 to 3 atmospheres. The gas phase heat feedback and the condensed-phase heat release help determine the extent of propellant response to a dynamic phenomenon. In order to understand this increase in response amplitude with an increase in pressure from 1 to 3 atmospheres, the mean and unsteady components of the gas-phase heat feedback, and the steady surface heat release are evaluated.

At 1 atmosphere, the maximum response amplitudes are 1.6 and 1.4 at 35 and 60 W/cm$^2$, and the gas-phase heat feedbacks are 4±1.3 and 2.5±0.95 W/cm$^2$. At 3 atmospheres, the maximum response amplitudes at the two laser fluxes are 2.0 and 1.8, with gas-phase heat feedbacks of 9.5±3.1 and 7.2±2.5 W/cm$^2$. Hence there is a substantial increase in the unsteady component of the gas-phase heat feedback. Since the pressure-driven experiments measure the thrust response of the propellant to the unsteady gas-phase heat feedback, an increase in the unsteady component of this heat feedback results in the higher response amplitudes.

The increase in response amplitude with pressure could also be due to the self-oscillatory decomposition mechanisms that exist in the condensed-phase of HMX. These decomposition mechanisms are evaluated in the next few paragraphs.

Brill and Brush found that there were multiple step reactions in the condensed-phase decomposition of HMX [108]. Thynell et al. simulated these experiments numerically with the assumption that the products from the two competing reactions were dissolved in
a liquid (foam layer) [109]. This suggested a buildup of NO₂ and CH₂O before an exothermic "runaway" occurred. The two-step reaction is as follows:

(A) HMX $\rightarrow$ HMX (intermediates)

(B) HMX (intermediates) $\rightarrow$ gas-phase products

The reactions result in the formation of intermediates through endothermic reactions followed by an exothermic runaway. With an increase in the ambient pressure, there is an increase in the amount of endothermic reactions resulting in a larger buildup of intermediates and lower temperatures. When the temperature and concentration of HMX (intermediates) reach a critical value, the exothermic reactions will occur and drive the temperature to a higher level. After the HMX (intermediates) are consumed, reaction B slows down and the temperature drops and allows a buildup of HMX (intermediates) through reaction A. At pressures used in this study, the exothermic reactions described in B do not supply enough heat to sustain pyrolysis resulting in some amounts of self-oscillatory combustion. Since these secondary reactions take place in the two-phase region, they may be pressure dependent. Hence with an increase in pressure from 1 to 3 atmospheres, the increase in the reaction rates of these exothermic reactions could result in greater exothermicity in the condensed-phase and higher surface heat release. The higher rates of endothermic and exothermic reactions at higher pressure would result in larger variations in temperature and hence larger variation in the burning rate. Table 5-2 shows that the increase in pressure increases the condensed-phase exothermic heat release. This suggests that the increase in pressure results in greater amounts of secondary exothermic reactions (reaction B) and is consistent with the postulate that the higher pressure-driven
response amplitudes at 2 and 3 atmospheres could be due to an increase in the gas-phase heat feedback coupled with the condensed-phase reaction channels for HMX.

This appears to be in contrast with the analytical model developed by Culick that suggested an increase in the exothermic reactions in the condensed-phase would result in lower response amplitudes. However it should be noted that the model used only a single parameter “P” to determine gas-phase effects on the condensed-phase response. Hence some effort was spent towards developing a better understanding of this model with emphasis on understanding the role of the “P“ and “Q” parameters. These efforts are documented in the next sub-section.

Table 5-2 and figures 5-18, 5-19 and 5-20 show that the pressure-driven response amplitudes increase with an increase in heat release in the surface reaction zone. The heat release increases from 38 cal/gm at 1 atmosphere, to 46 cal/gm at 3 atmospheres at 35 W/cm², while the maximum response amplitude increases from 1.6 at 1 atmosphere, to 2.0 at 3.0 atmospheres. At 60 W/cm², the heat release increases from 34 to 39 cal/gm, and the response amplitude increases from 1.4 to 1.85 with the increase in pressure from 1 to 3 atmospheres. The increase in pressure-driven response amplitudes with an increase in condensed-phase heat release appears to be consistent independent of the laser flux. At 3 atmospheres with a laser flux of 60 W/cm², the heat release is 39 cal/gm and the pressure-driven response amplitude is 1.83, while at 2 atmospheres and a laser flux of 35 W/cm², the heat release is 42 cal/gm and the response amplitude is 1.87. This gas-phase heat feedback and the condensed-phase heat release are nearly identical at 2 atmospheres and a laser flux of 35 W/cm², and 3 atmospheres and a laser flux of 60 W/cm². This
suggests that the response amplitudes are similar for similar values of the condensed-phase heat release and gas-phase heat feedback.

### 5.2.2.2 Comparison with analytical models

In 1967 Culick developed an analytical model that considered the effect of sub-surface decomposition reactions in the formulation of the response function [6]. The formulation considered the heat generation per unit volume took place in a region just below the propellant surface and presented it in a non-dimensional form given in equation 5.18. The spatial co-ordinate is expressed in equation 5.19

\[
\dot{Q} = \frac{\dot{Q}_d \lambda_p}{T_s (mc)^2} \tag{5.18}
\]

\[
\xi_p = \frac{m cx}{\lambda_p} \tag{5.19}
\]

where \(m\) is the mass flux, \(c\) is the specific heat, \(\lambda\) is the thermal conductivity, and \(Q_d\) is the heat release per unit volume.

After much algebraic manipulation, equation 5.20 was derived which can be used to determine the real part of the response function.

\[
\frac{1}{n} \cdot \mu \cdot \frac{\mu}{\varepsilon} = \frac{D \left[ P - \left( \frac{E}{n} \right) \left( X_p + X_{p-\tau} \right) \right] \left( X_{\tau-\tau} \right) \left( X_{p-\tau} \right) + n_s}{n} \tag{5.20}
\]

Some non-dimensional parameters will be converted into dimensional form to allow an easier comparison with the relevant experimentally measured parameters.
\[ E_s = \frac{RT_s}{1-T_s/T_i} \cdot \text{Acal / mol} \]  

(5.21)

\[ x\dot{Q}_x = \frac{(\bar{m}c)^2 T_i}{(\bar{m}c)} \cdot (lQ) = \text{cal / cm}^2 - \text{sec} \]  

(5.22)

\[ x = \frac{\lambda_p \cdot l}{\bar{m}c} \]  

(5.23)

A Q value of 1.5 corresponds to a sub-surface decomposition value of 30 cal/gm. Table 5-2 shows that the experimentally determined heat release in the sub-surface region is 38 cal/gm. Hence a Q value near 2 gives the “correct” amount of heat release in the sub-surface region and should result in response functions that are similar to the experimental data. These equations were programmed into a simple Fortran code and used to perform some parametric studies on the effects of the heat release, gas-phase and width of the decomposition region in the condensed-phase.

Figure 5-21 plots the real part of the response function for HMX at 101 kPa and a laser flux of 35 W/cm² with data obtained from equation 5-20. In addition to comparing the experimental and analytical response functions, the figure plots a range of Q values from 1.5, to 4 to illustrate the effect of sub-surface decomposition on the real part of the response function. There are two important conclusions that can be drawn from the model

a) Though the analytical model is a substantial improvement over the FM model, it still under predicts the experimental measured response and cannot be used to make any quantitative predictions of the behavior of the response function.
b) An increase in the sub-surface decomposition reactions results in a lower real part of the response function

Figure 5-21 Comparison of experimental response for HMX with Culick’s response function
Conclusion b holds true when the Q parameter is changed at a given test condition without changing the gas-phase “P” parameter. This P parameter is dependent on the non-dimensional activation energy, the burning rate exponent and an arbitrary parameter. This arbitrary parameter is dependent on the surface and flame temperatures and the activation energy for the reactions in the flame region. Changes in the surface and flame temperatures with the increase in pressure will affect this parameter. Figure 5-22 plots the response for two different heat release and gas-phase parameters. The figure shows that the response function can increase with an increase in exothermic reactions in the condensed-phase if it is accompanied by a suitable change to the gas-phase parameter.
Hence the increase in the pressure-coupled response functions for HMX with the increase in exothermic heat release in the condensed-phase can be qualitatively consistent with this analytical model. It has been noted that there is little change in the surface and flame temperature for HMX with the increase in pressure from 1 to 3 atmospheres. Hence realistic changes in the P parameter are not quite as large as shown in figure 5-21. Clearly there are many assumptions in this analytical model that make it difficult to compare it to measured response amplitudes. One of the main drawbacks is the Arrhenius-type surface pyrolysis law that is used to relate burning rate and surface temperature. Hence an effort was made to use the analytical treatment developed by Iribicu and Williams in 1975 [34]. Roh et al. have used this technique to obtain an instantaneous burning rate [48]. The formulation is based on the following equations for the condensed phase.

**Energy Equation**

\[
\rho_c C_c \frac{\partial T}{\partial t} + \dot{m} C_c \frac{\partial T}{\partial x} = \lambda_c \frac{\partial^2 T}{\partial x^2} + H \dot{\omega} \tag{5.24}
\]

where subscript c denotes the condensed phase, \( \omega \) is the rate of thermal decomposition, \( \lambda \) is the thermal decomposition, and \( \dot{m} \) the mass flux.

**Propellant Mass**

\[
\rho_c \frac{\partial Y}{\partial t} + \dot{m} \frac{\partial Y}{\partial x} = -\dot{\omega} \tag{5.25}
\]

where \( Y \) is the propellant mass fraction.

A zeroth order reaction is used to denote the propellant decomposition and is given by equation 5.26.
\[
\dot{\omega} = \rho_c A_c \cdot \exp \left( -\frac{E_c}{RT} \right)
\]

(5.26)

The main processes in this layer are thermal diffusion and condensed-phase reaction that are defined by the following length scales.

\[
\frac{\alpha_c}{r_b} = \frac{\lambda_c}{m C_c}
\]

\[
\frac{\lambda_c}{m C_c \beta} \text{ where } \beta = \frac{E_c}{RT_s}
\]

where \( \alpha \) is the thermal diffusivity, \( r_b \) is the propellant burning rate, and \( \beta \) is the dimensionless activation energy.

A non-dimensional length and temperature scale are defined in equation 5.27 and 5.28.

\[
\eta = -\frac{\beta m C_c}{\lambda_c} x
\]

(5.27)

\[
\zeta = \beta \frac{T_x - T}{T_s}
\]

(5.28)

Using the non-dimensional variables, and assuming the processes in the foam layer to be quasi-steady, equations 5.24 and 5.25 can be written as

\[
\frac{d^2 \zeta}{d\eta^2} + \frac{1}{\beta} \frac{d\zeta}{d\eta} = h \Lambda \exp \left( -\frac{\zeta}{\beta} \right)
\]

\[
\left\{-\frac{\zeta}{1 - \frac{\zeta}{\beta}}\right\}
\]

(5.29)
$$\frac{dY}{d\eta} = \Lambda \exp \left( \frac{-\zeta}{1 - \frac{\zeta}{\beta}} \right)$$  \hspace{1cm} (5.30)$$

where \( h = H/C_c T_s \), and

$$\Lambda = \frac{\rho_c A \lambda_c}{\beta h n^2 C_c} \exp(-\beta)$$

The \( \Lambda \) parameter is the non-dimensional burning rate parameter.

Boundary Conditions

The propellant is assumed to be fully decomposed at \( \eta = 0 \) and hence can be described as

$$Y(0) = \zeta(0) = 0$$  \hspace{1cm} (5.31)

$$\left[ n h_s - \lambda_c \frac{\partial T}{\partial x} \right]_{\eta=\infty} = \left[ n h_g - \lambda_g \frac{\partial T}{\partial x} \right]_{\eta=0}$$  \hspace{1cm} (5.32)

the heat release in this layer can be described as

$$Q_s(T_s) = h_s - h_g = C_c T_s + \Delta h_{f,c}^o - C_p T_s - \Delta h_{f,g}^o$$  \hspace{1cm} (5.33)

Using equations 5.27 and 5.28 in equations 5.32 and 5.33 we get

$$\left( \frac{d\zeta}{d\eta} \right)_{\eta=\infty} = \left( \frac{d\zeta}{d\eta} \right)_{\eta=0} + \frac{Q_s}{C_c T_s}$$  \hspace{1cm} (5.34)

For HMX, the activation energy is approximately 42 Kcal/mol and the surface temperature is about 650 K. Hence \( \beta >> 1 \). This allows simplification of equation 5.29 and 5.30 into 5.35 and 5.36.

$$\frac{d^2 \zeta}{d\eta^2} = h \Lambda \exp(-\zeta)$$  \hspace{1cm} (5.35)
\[
\frac{dY}{d\eta} = \Lambda \exp(-\zeta)
\] (5.36)

The first integrals of 5-35 and 5-36 yield

\[
\Lambda = \left( \int_{0}^{\infty} \exp(-\zeta) d\eta \right)^{-1}
\] (5.37)

\[
\frac{\left( \frac{d\zeta}{d\eta} \right)^2}{2} = \frac{(C + h)^2}{2} - h\Lambda \exp(-\zeta)
\] (5.38)

Equations 5.37 and 5.38 yield

\[
\Lambda = c + h/2
\] (5.39)

\[
\left( \frac{\partial \zeta}{\partial \eta} \right)_{\eta=0} = c + h
\]
where \[
\left( \frac{\partial \zeta}{\partial \eta} \right)_{\eta=0} = c
\]

\[
\frac{Q_s}{C \cdot T_s} = h
\]

In a dimensional form, 5.39 can be expressed as follows

\[
r_b^2 = \alpha \left( \frac{A \exp(-\beta)}{\beta} \right)^1
\] (5.40)

where \( r_b \) is the instantaneous burning rate, \( A \) is the pre-exponent in the decomposition reactions for HMX, and \( \alpha \) is the thermal diffusivity.

To use the above equation, dynamic surface temperature measurements were obtained. These measurements are extremely difficult and hence were limited to very
few driving frequencies. The steady-state modeling work described in section 5.1.3 was used to predict the gas-phase heat feedbacks.

![Figure 5-23](image-url)

**Figure 5-23** Surface temperature during pressure-driven combustion at 101 kPa

Figure 5-23 plots the surface temperature measured during pressure-driven combustion of HMX at 101 kPa and a laser flux of 35 W/cm². The figure shows the variation in surface temperature at a driving frequency of 4 Hz. The surface temperature varies between a maximum of 675 K and a minimum of 615 K. Gas-phase temperature profiles along with numerical computations through CHEMKIN predict the gas-phase
heat feedback at the surface to be about 3.1 and 2.3 W/cm². This heat feedback is plugged into equation 5-40 to obtain the instantaneous burning rates. The key constraint lay in accurate use of the pre-exponent of the condensed-phase thermal decomposition reaction. As documented in equations 5-4,5-5 and 5-6, HMX undergoes two global decomposition pathways. In order to obtain an “accurate” number for the pre-exponent, the surface temperatures and reaction rates from table 5-3 were used as weighting functions to obtain a “reasonable” pre-exponent. The same logic was used to obtain activation energy for the decomposition reaction.

This analysis predicted burning rates fluctuations of 0.065 mm/s at a mean burning rate of 0.63 mm/s. This resulted in a response amplitude of 1.01 as compared to the experimentally measured amplitude of 1.33. This analysis appears to provide the best agreement with the experimental data. This is largely due to the fact that the condensed-phase reactions, gas-phase heat feedback and surface temperature effects are considered in the development of the equation. However, this simplified calculation relied heavily on experimental inputs to obtain the burning rate. Such experimental measurements are extremely difficult at higher pressures and oxidizing environments and cannot be performed at all conditions for all propellants. Hence this suggests that a rigorous numerical code is essential to obtain predictive response functions.

5.2.3 Comparison of laser and pressure-driven response amplitudes

5.2.3.1 Comparison at atmospheric pressure
Figure 5-24 presents a comparison between laser and pressure-driven combustion response at laser fluxes of 35 and 60 W/cm². The figure shows that the response peaks appear to lie between Ω values of 12 and 15. The response amplitudes for pressure-driven combustion are higher than the amplitudes for laser-driven combustion for both heat flux cases. Also, the increase in heat flux decreases the response amplitude during pressure driven combustion, but does not appear to affect the response amplitude during laser-driven combustion.

Figure 5-24 Comparison of Thrust Response Amplitudes versus Ω during Laser and Pressure-Driven combustion of HMX.
In order to understand the different behavior of the laser and pressure-driven combustion response amplitudes with a change in laser flux, the effect of the mean laser flux on surface temperature and gas-phase heat feedback was evaluated.

Figure 5-1 and table 5-1 show that the increase in laser flux from 35 to 60 W/cm$^2$ has a negligible effect on surface temperature (an increase of 5 K). As discussed in section 5.1.1, the primary effect of an increase in laser flux is the increase in burn rate and flame standoff distance and a resultant decrease in heat feedback. The steady gas-phase heat feedbacks are about 3 and 2 W/cm$^2$ at laser fluxes of 35 and 60 W/cm$^2$ respectively.

During laser-driven combustion, the laser is modulated at amplitudes of $\pm 15$ W/cm$^2$. Since the laser is modulated at an energy level that is much higher than the gas-phase heat feedback, the laser-driven combustion response measurements are primarily condensed-phase responses to the unsteady laser flux. Since the condensed phase behavior is not significantly altered by the increase in mean laser heat flux and the unsteady gas-phase heat feedback is overwhelmed by the unsteady laser flux, the condensed-phase response does not change with the increase in mean laser flux during laser-driven combustion. Table 5-4 shows that there is a very small change in the net unsteady flux that is incident on the propellant surface resulting in very little change in the propellant response amplitudes with the increase in laser flux.

During pressure-driven combustion, the variation in ambient pressure results in a change in the flame standoff distance and gas-phase heat feedback. During pressure-driven combustion, the gas-phase heat feedback is the driving mechanism and variation in this heat feedback results in a variation in the burning rate (thrust in this study). The
higher laser flux increases the flame standoff distance and decreases the gas-phase heat feedback and decreases the condensed-phase response amplitudes at the higher laser flux. Table 5-6 shows that the mean and unsteady components of the gas-phase heat feedback decrease with the increase in pressure. Since the propellant condensed-phase responds to this unsteady heat feedback, a decrease in this heat feedback results in the lower response amplitude.

In order to determine the reasons for the higher response amplitudes during pressure-driven combustion compared to laser-driven combustion, the relationship between thrust and burning rate was examined. The unsteady thrust equation is obtained by perturbing equation 5.15 for mass flux and neglecting the effect of fluctuation in the flame temperature. This assumption is valid for propellants like HMX [105].

\[
\tau' = 2\bar{m}'\left(\frac{RT_f}{PM}\right)
\]  

(5.41)

The burning rate, propellant density and gas density expressed in equation 5.42 are used to obtain the relationship between unsteady thrust and the pressure exponent and is expressed in equation 5.43.

\[
r_b = bp^n, \quad \frac{1}{\rho_{gas}} = \left(\frac{RT_f}{PM}\right), \bar{m} = \rho_p \cdot r_b
\]

(5.42)

\[
\tau' = \frac{2\rho_p \cdot \left(bp^n\right) \cdot \left(n \cdot \frac{p'}{p}\right) \cdot \left(bp^n\right)}{\rho_{gas}}
\]

(5.43)

Clearly the unsteady thrust is dependent on the pressure exponent and equation 5.44 shows the effect of a pressure increase from 1 to 2 atmospheres on the unsteady thrust
response. Equation 5.44 is obtained with the assumptions that the pressure exponent, propellant density and the final flame temperatures do not change with pressure.

\[
\frac{\tau'(2\text{atm})}{\tau'(1\text{atm})} \equiv 2^{(2-n-1)}\tag{5.44}
\]

Equation 5.44 suggests that propellants with a pressure exponent above 0.5 will show larger response amplitudes with an increase in pressure. The pressure exponent of HMX at one atmosphere is 0.8 [15]. Hence the higher response amplitudes during pressure-driven combustion are partially due to the increase in chamber pressure from 1 to 1.5 atmospheres. Clearly the laser and pressure-driven experiments use different driving mechanisms and may not provide the same amplitude and phase response even at identical pressures.

### 5.2.3.2 Comparison at higher pressures

Figure 5-25 (a) and (b) plot the laser and pressure-driven response amplitudes for HMX at a laser flux of 35 W/cm\(^2\) at pressures of 101, 202 and 303 kPa. The peak response amplitudes are observed at non-dimensional frequencies of 12-15 for both laser and pressure-driven measurements. The nearly constant value of the non-dimensional frequency at the various pressures clearly suggests that the peak response amplitude is a function of the condensed-phase thermal relaxation. It is also important to note that the response amplitudes do not exactly scale to the non-dimensional frequency and suggests that QSHOD may not be a perfect match to the real situation. Figure 5-25 (a) shows that
the maximum pressure-driven response amplitude increases from 1.65 at 101 kPa, to 1.8 at 202 kPa and then to 2.0 at 303 kPa, while figure 5-25 (b) shows that the maximum laser-driven response amplitude decreases from 1.25 at 101 kPa, to 1.15 at 303 kPa. Clearly the effect of ambient pressure is different on the laser and pressure-driven experiments. This has been discussed in detail in the previous sections pertaining to laser and pressure-driven experiments and will only be summarized briefly.

It has been established that at a given pressure, the gas-phase heat feedback is out of phase with the laser flux. Hence the increase in the laser flux decreases the gas-phase heat feedback. At a laser flux of $35 \text{ W/cm}^2$ and a pressure of 1 atmosphere, the gas-phase heat feedback is $3 \text{ W/cm}^2$ while at 3 atmospheres, the gas-phase heat feedback is $8 \text{ W/cm}^2$. Table 5-5 shows that the increase in pressure reduces the unsteady net flux that is incident on the surface. The net flux is defined as the difference between the laser flux and the gas-phase heat feedback. Since the laser-driven experiments are condensed-phase response to this net flux that decreases with an increase in pressure, the response amplitude also decreases with the increase in pressure. There is only a small decrease in the response amplitude because the larger unsteady laser flux tends to mask the effect of pressure on the unsteady gas-phase heat feedback.

During pressure-driven combustion, a steady laser flux is used while the ambient pressure is varied. The ambient pressure varies at 10% (peak-to-peak) of the mean pressure at the selected frequency. Sections 5.1.1 and 5.2.3 discussed the effect of the higher pressure on the flame standoff distances and the mean and unsteady gas-phase
heat feedback. Since the pressure increase resulted in higher unsteady components of the
heat feedback, the response amplitude also increased with pressure.

These experiments show that the driving mechanisms for the laser and pressure-driven experiments are different and do not exhibit similar trends with variation in the ambient pressure.
Figure 5-25 Response Amplitudes for HMX at 35 W/cm² and 101, 202 and 303 kPa.
Figures 5-26 compares the laser and pressure-driven response amplitudes for HMX at 60 W/cm$^2$ at pressures of 101, 202 and 303 kPa. Once again the maximum pressure-driven response amplitude increases from 1.4 at 101 kPa, to 1.8 at 303 kPa, while the laser-driven response amplitudes decreases from 1.2 at 101 kPa, to 1.1 at 303 kPa. These experiments are consistent with the results obtained at 35 W/cm$^2$. The gas-phase heat feedbacks at these conditions are 2 and 6 W/cm$^2$ at 101 and 303 kPa respectively. The gas-phase heat feedback is lower at the higher heat flux and results in lower maximum response amplitudes.

The pressure and laser-driven response measurements at 35 and 60 W/cm$^2$ are remarkably consistent and clearly show that the increase in pressure and gas-phase heat feedback increases the pressure-driven response amplitudes but decreases the laser-driven response amplitudes. Since the peak response amplitudes are observed at almost the same value of non-dimensional frequency of 12 for all test cases, the maximum response amplitude during both laser and pressure-driven combustion is clearly a function of the condensed-phase thermal relaxation time.
Figure 5-26 Response Amplitudes for HMX at 60 W/cm$^2$ and 101, 202 and 303 kPa.
5.2.4 **Comparison of experimental response with a theoretical function**

Son and Brewster at the University of Illinois used the ZN model to obtain an expression for \( R_p \) (equation 2.13) and \( R_q \) (equation 2.14) with a laser flux incident on the propellant surface [38,39,40,41]. Son et al. believe that it is possible to use a transfer function to relate the laser and pressure-driven response functions through a transfer function. In order to do this, they use appropriate ZN parameters and ratio the pressure and laser-driven response functions described in equations 2.13 and 2.14. The objective here is to compare the experimentally obtained response functions against the predictions of Son et al. for HMX. Such a comparison will help validate or disprove the possibility of using a transfer function and relatively easy laser-driven response experiments to obtain a pressure-driven response function.

The transfer function is defined as the ratio of pressure-driven response to the laser-driven response and is given by equations 5-22 and 5-23. Table 5-8 shows the values that were used for the ZN parameters. The parameters were obtained from experimental data based on the equations defined by Son et al and Loner et al. [38,106]. The \( \nu^* \), \( \nu_q \), \( \delta^* \) and \( \delta_q \) values are all observed to be invariant with heat flux and pressure.

\[
TF = \frac{R_p}{R_q} = \frac{\nu^* + \delta^* \cdot (\lambda - 1)}{\nu_q + \delta_q \cdot (\lambda - 1)} - \frac{k^* f_r J \cdot (\lambda - 1)}{\beta_r + \lambda - 1} \left\{ 1 + (\lambda - 1) \cdot \frac{r^* - k^* (\beta_r - 1 + \lambda + f_r J)}{\lambda \cdot (\beta_r - 1 + \lambda)} \right\} \left\{ 1 + (\lambda - 1) \cdot \frac{r^* - k^* (\beta_r - 1 + \lambda + f_r J)}{\lambda \cdot (\beta_r - 1 + \lambda)} \right\} \right\}
\] (5-22)
Figure 5-27 shows a plot of the transfer function of Son et al. and the ratio of experimental pressure and laser driven response functions at heat fluxes of 35 and 60 W/cm$^2$ at a pressure of 101 kPa. This transfer function predicts a value of 1 while the experimental ratios of the pressure and laser-driven response functions are 1.3 at low values of $\Omega$. The transfer function gradually decreases from 1 to 0.8 at an omega of 180. At 35 W/cm$^2$, the experimental ratio increases from 1.3 at an omega of 12, to 1.5 at an omega of 100 and then drops off to 1.4 at 180. At 60 W/cm$^2$, the ratio decreases from 1.3 at an omega of 7, to 1.2 at an omega of 30 and then increases to 1.5 at an $\Omega$ of 100. The figure shows that the theoretical transfer function developed by Son and Brewster under predicts the experimental data particularly at the lower and higher frequency regimes. However, the theoretical transfer function can be assumed to provide reasonable agreement with the experimental response functions for laser and pressure-driven combustion. At high frequency, the quasi-steady assumptions are invalid and hence the transfer function curve above an $\Omega$ of 100 requires careful interpretation.
<table>
<thead>
<tr>
<th></th>
<th>101 kPa</th>
<th>202 kPa</th>
<th>303 kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35 W/cm²</td>
<td>60 W/cm²</td>
<td>35 W/cm²</td>
</tr>
<tr>
<td>( \nu )</td>
<td>0.84</td>
<td>0.84</td>
<td>0.84</td>
</tr>
<tr>
<td>( \nu_q )</td>
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<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>( \delta )</td>
<td>-0.031</td>
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<td>-0.031</td>
</tr>
<tr>
<td>( \delta_q )</td>
<td>-0.022</td>
<td>-0.022</td>
<td>-0.022</td>
</tr>
<tr>
<td>( k )</td>
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<td>1.13</td>
<td>1.13</td>
</tr>
<tr>
<td>( J )</td>
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<td>0.45</td>
<td>0.26</td>
</tr>
<tr>
<td>( Br )</td>
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<td>56.7</td>
<td>56.7</td>
</tr>
<tr>
<td>( f_r )</td>
<td>0.011</td>
<td>0.033</td>
<td>0.034</td>
</tr>
</tbody>
</table>

Table 5-8. A list of the ZN parameters used in the theoretical transfer function.
The transfer function is plotted with the experimental ratios of pressure and laser-driven response at 202 kPa in figure 5-28. The transfer function predicts a ratio of 1 at low frequency that decreases to 0.9 at an omega of 100. The experimental ratio at a laser flux of 35 W/cm², is 1.6 at an omega of 7, it then increases and plateaus to 1.8 at an omega value of 60 and higher. The experimental ratio at 60 W/cm² is 1.7 at an omega of 4 and then decreases to 1.5 at an omega value of 75. A straight line with zero slope and an offset of 1.6 can be used to fit the experimental ratios at 35 and 60 W/cm² within the experimental uncertainty. Clearly the transfer function is under-predicting the experimental ratios of pressure and laser-driven combustion at all frequencies and does
not appear to be a reasonable approximation that can be used to relate laser and pressure-driven combustion.

Figure 5-28 Transfer function and ratio of response functions versus $\Omega$ at 202 kPa

Figure 5-29 compares the transfer function to the experimental ratios of pressure and laser-driven combustion at 303 kPa and laser fluxes of 35 and 60 W/cm$^2$. The transfer function once again predicts a small decrease in ratio from 1.05 to 1.0 with an increase in the $\Omega$ value from 3 to 70, while the experimental ratio at a laser flux of 35 W/cm$^2$ increases from 1.75 at an omega value of 3, to 2.0 at an omega value of 70. Clearly the transfer function greatly under predicts the ratio of the pressure and laser-driven response
functions at both heat fluxes and would not serve as a reasonable approximation to relate laser and pressure-driven response data.

It should be noted that there is scatter in the experimental data and hence all the experimental ratios can be plotted as straight lines with zero or small positive slopes. This will allow qualitative agreement between the experimental data and the theoretical transfer function. The author recommends that the transfer function be discarded as a possible method to approximate between laser and pressure-driven response functions. It may be possible to obtain such a function at a later date via improvements to the methodology namely the ZN framework.

![Graph](image)

**Figure 5-29** Transfer function and ratio of response functions versus Ω at 303 kPa
Chapter 6

RESULTS AND DISCUSSION: AP COMPOSITE PROPELLANTS

This chapter is divided into five sections. Each section will cover data for the three classes of AP composite propellants- namely: the MURI 4 and 5 propellants, the AP/energetic binder propellants and the AP/HTPE and AP+AN/HTPE propellants. Section 1 will focus on the steady-state measurement and analyses of burning rate, temperature and heat release. Section 2 and 3 discuss the unsteady laser and pressure-driven thrust response profiles for the three classes of propellants, while section 4 covers the comparison of the laser and pressure-driven response amplitudes. Section 5 attempts to use a transfer function to relate laser and pressure-driven combustion, while section 6 uses a modified burning rate equation to obtain response amplitudes.

6.1 Steady State Analysis

This section focuses on the steady-state measurements and analyses of the propellants under various test conditions. The temperature profiles are used to obtain a gas-phase heat feedback and the surface temperatures are used to obtain a condensed-phase heat release. Measured species profiles are plotted against numerically predicted values for an AP/HTPB model to establish the validity of the chemical mechanism. The
validated model is used to calculate the effect of burning rate on gas-phase species profiles. This helps establish the effect of heat flux on gas-phase combustion behavior of AP/HTPB propellants.

6.1.1 Temperature Measurements

The temperature profiles for the AP based composite propellants were derived by piecing together available temperature data from separate experiments. The surface temperature was monitored by attaching a 10 µm platinum/platinum-rhodium thermocouple directly to the regressing surface. During tests, the thermocouple was always attached to the surface due to the weight of small nuts placed on the wires as explained in Chapter 3. Chromel/Alumel, Tungsten/Rhenium and Platinum/Rhodium thermocouples were used in the measurements. In order to use the platinum/rhodium and tungsten/rhenium thermocouples, argon was used as the ambient gas. This helped reduce the oxidation of the thermocouple wires and increase its lifespan.

Due to the heterogeneous nature of these AP composite propellants, the thermocouple junction point could lie on an AP particle or on the inert binder or partially on both during surface temperature measurements. This leads to three different surface temperature measurements and hence very large standard deviations. Zenin states that the structure of AP composite propellants with coarse AP (sizes above 100 µm) is complicated due to dissimilarities in the macro-kinetic characteristics of AP and the binder particles [101]. The temperatures of the AP particles and the binder are different and result in multi-dimensional combustion processes at the propellant surface. However AP composite propellants with fine AP particles show interaction between the AP
decomposition products and the binder resulting in one-dimensional surfaces. In this study, the author assumes that the large standard deviation is caused by particle size effects and will treat the propellant surface as one-dimensional.

Due to the relatively poor spatial resolution in the condensed-phase of the AP composite propellants, the temperature profiles cannot be used to obtain a heat release parameter ($\phi$) as a function of spatial distance or temperature. As a result, a global one-dimensional energy analysis is used to obtain the heat release in the surface reaction zone. Since the technique has been described in section 5.1.3, only numerical values will be presented. The heat release is used to analyze the effects of exothermic reactions on the unsteady laser and pressure-driven response amplitudes.

6.1.1.1 MURI Propellants
Figure 6-1 plots the temperature profiles for MURI 4 at 1 atmosphere during self-deflagration and laser-assisted combustion at 35 and 60 W/cm². The profiles are very similar to each other and appear to overlap each other from the sub-surface to the final flame region. The surface temperature for the propellant is 720, 750 and 775 K during self-deflagration and laser assisted combustion at 35 and 60 W/cm² respectively. The condensed-phase profile shows a distinct gradient change around 500 K for all three cases. This gradient change is associated with the change of the AP particles from an orthorhombic to a cubic structure. As mentioned earlier, the smallest successful
thermocouple measurements used 10 µm junctions and with this relatively poor spatial resolution, the shift in the location of gradient change in the condensed-phase due to laser flux was not detected. The increase in laser flux does result in an increase in burning rate and surface temperature and should result in steeper condensed-phase temperature profiles. These profiles are quite consistent with the condensed-phase temperature profiles measured by Zanotti et al. who measure a transition thickness of 60 µm and a surface temperature of 750 K during self-deflagration [107].

The temperature gradients in the near-surface region are of the order of $4 \times 10^4$ K/cm. These large temperature gradients coupled with very high final flame temperatures ($\sim 3000$ K) result in poor repeatability in gas-phase temperature data. The highly oxidizing species produced in AP combustion resulted in oxidation of the thermocouple wires and produced erroneous results in the final flame region. Since the focus of these measurements was to establish the gas-phase heat feedback, the temperature measurements focused on the near-surface gas-phase regions and no efforts were expended towards use of coated thermocouples. The final flame temperatures of such propellants are best measured through non-intrusive techniques.

Figure 6-2 compares the temperature profiles for MURI 4 and 5 at 1 atmosphere during self-deflagration. The surface temperatures for the MURI 4 and 5 propellants at 1 atmosphere were 720 and 710 K respectively. The uncertainties in these measurements are of the order of $\pm 60$ K and suggest that the surface temperatures are nearly identical at these test conditions. The figure shows that the condensed and gas-phase temperature profiles are also very similar. Due to the experimental difficulties in obtaining
temperature profiles, temperature measurements were restricted to MURI 4 propellants with the assumption that the profiles would be similar for both MURI 4 and 5 propellants.

![Temperature Profile Graph](image)

**Figure 6-2** Comparison of temperature profiles for MURI 4 and 5 at 1 atmosphere during self-deflagration

Table 6-1 plots the burning rates and surface temperatures as a function of heat flux for MURI 4 and 5. The two propellants have similar percentages of AP and HTPB but contain different curing agents. The large uncertainties in the surface temperature measurements are due to the heterogeneous nature of the propellants. The different particle sizes and the inert binder matrix result in scatter in the data and large standard deviations. The burning rate measurements show that for the MURI 4 propellants, there is an increase in burning rate from 1.35 mm/s during self-deflagration, to 1.75 mm/s at a laser flux of 60 W/cm². For the MURI 5 propellants, the burning rate increases from 1.30
mm/s during self-deflagration, to 1.70 mm/s at a laser flux of 60 W/cm$^2$. The similar burning rates and temperature profiles for MURI 4 and 5 shows that there appears to be no effect of the different curatives on the steady-state behavior of these propellants at low pressures.

<table>
<thead>
<tr>
<th>Propellant</th>
<th>Incident Heat Flux (W/cm$^2$)</th>
<th>Average Burn rate (mm/sec)</th>
<th>Surface Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MURI#4</td>
<td>0</td>
<td>1.35±0.10</td>
<td>720±60</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>1.50±0.10</td>
<td>750±60</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.75±0.14</td>
<td>775±60</td>
</tr>
<tr>
<td>MURI#5</td>
<td>0</td>
<td>1.30±0.10</td>
<td>710±60</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>1.45±0.08</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.70±0.15</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6-1 – Burn rate and surface temperature data for MURI propellants at one atmosphere.

Figure 6-3 plots the temperature profiles for MURI 4 at 1, 2 and 3 atmospheres. The figure clearly shows that there is an increase in surface temperature from 720 K at 1 atmosphere, to 805 K at 3 atmospheres. Another interesting result is the condensed-phase thermal profile. The condensed-phase thermal profiles have larger gradients and shorter thermal penetration depths with the increase in pressure. Due to poor spatial resolution, these trends should only be examined qualitatively.
Figure 6-3 Temperature profiles for MURI 4 at 1, 2 and 3 atmospheres during self-deflagration.

Table 6-2 lists the burning rates and surface temperatures for MURI 4 at 1, 2 and 3 atmospheres during self-deflagration. The table shows the increase in burning rate from 1.35 mm/s to 2.1 mm/s with the increase in pressure, while the surface temperature increases from 720 to 805 K with the increase in pressure from 1 to 3 atmospheres.

The steady state data burning rate and surface temperatures were fitted to equations 6.1 and 6.2. The burning rate and surface temperature at 1 atmosphere were taken as the reference data and produced a ‘n’ of 0.42 and a ‘nTs’ value of 0.1.

\[
\bar{r}_b = r_{b, ref} \left( \frac{p}{p_{ref}} \right)^n
\]

(6.1)
\[ \bar{T}_s = T_{s,\text{ref}} \left( \frac{p}{p_{\text{ref}}} \right)^{n_{T_s}} \] (6.2)

<table>
<thead>
<tr>
<th></th>
<th>101 KPa</th>
<th>202 KPa</th>
<th>303 KPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burning rate (mm/s)</td>
<td>1.35±0.10</td>
<td>1.8±0.15</td>
<td>2.1±0.20</td>
</tr>
<tr>
<td>Surface Temperature (K)</td>
<td>720±60</td>
<td>770±70</td>
<td>805±70</td>
</tr>
<tr>
<td>( n )</td>
<td>0.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n_{T_s} )</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6-2 – Burn rate and surface temperature data for MURI 4 at one, two and three atmospheres.

Zanotti et al. used a reference temperature of 945 K at 30 atmospheres and reported a ‘\( n_{T_s} \)’ of 0.045 [107]. If these values of reference temperature and pressure are used as a reference, the present data gives ‘\( n_{T_s} \)’ of 0.06. Within the large standard deviations associated with surface temperature measurements, these values are quite similar and suggest that the MURI 4 propellant displays characteristics that are consistent with a typical AP/HTPB propellant.

Figure 6-4 is an image of laser assisted combustion experiments on MURI 4 at 1 atmosphere at a laser flux of 35 W/cm². The image shows the absence of a flame standoff distance. Hence the temperature gradients are very large in the near-surface region and present challenges in accurate and repeatable measurement of the gas-phase temperature profile. The propellant flame does not appear to be affected by the changes in laser flux. The large uncertainties in the gas-phase heat feedback also make it difficult to observe the effects of laser flux on the gas-phase heat feedback.
6.1.1.2 AP/Energetic Binder Propellants

The second set of propellants that were tested used energetic binders instead of the relatively inert HTPB. Some of the components of this energetic binder produce large amounts of condensed-phase heat release resulting in higher surface temperatures. Table 6-3 lists the burning rates and surface temperatures for the AP/energetic binder propellant at one atmosphere. The table shows that the surface temperatures of 920, 955 and 975 K are much higher than the temperatures for the MURI 4 and 5 propellants. The burning rates are 1.75 and 2.30 mm/s during self-deflagration and laser-assisted combustion at 60 W/cm². These burning rates and surface temperatures are higher than the AP/HTPB
propellants and suggest that the presence of the binder results in greater amounts of exothermic reactions in the condensed-phase and hence higher burning rates and higher surface temperatures.

<table>
<thead>
<tr>
<th>Incident Heat Flux (W/cm²)</th>
<th>Burning rate (mm/sec)</th>
<th>Surface Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.75±0.10</td>
<td>920±80</td>
</tr>
<tr>
<td>35</td>
<td>2.05±0.15</td>
<td>955±80</td>
</tr>
<tr>
<td>60</td>
<td>2.30±0.20</td>
<td>975±80</td>
</tr>
</tbody>
</table>

Table 6-3 Burning rates and surface temperatures for the AP/energetic binder propellant

Figure 6-5 Temperature profiles for AP/energetic binder propellant at 1 atmosphere during self-deflagration and laser-assisted combustion at 35 and 60 W/cm².
Figure 6-5 shows the temperature profiles for the AP/energetic binder propellant at 1 atmosphere during self-deflagration and laser-assisted combustion at 35 and 60 W/cm². The profiles at the three conditions are very similar. The gas-phase temperature gradients are $10^5$ K/cm and are larger than the AP/HTPB propellants ($4 \times 10^4$ K/cm). Clearly the presence of the energetic binder had resulted in higher burning rates and larger condensed and gas-phase temperature gradients. These large temperature gradients coupled with the highly oxidizing species produced in AP combustion, resulted in oxidation of the thermocouple wires and produced erroneous results in the final flame region. Hence experiments primarily focused on measurement of the condensed and near-surface, gas-phase temperatures.

The figure shows that the increase in laser flux appears to result in larger temperature gradients in the condensed-phase and smaller thermal penetration depths. The larger temperature gradients could be due to greater exothermicity in the condensed-phase. The poor spatial resolution in the condensed-phase prevents the possibility of obtaining a heat release parameter as a function of spatial distance or temperature by solving the heat conduction equation. This has also been noted by Zenin et al [101]. Hence, the surface and initial temperatures are used to determine the total heat released in the surface reaction zone. The increase in laser flux increases the surface temperature from 920 K during self-deflagration, to 975 K at a laser flux of 60 W/cm². Clearly the presence of the energetic binder has resulted in higher surface temperatures.

Figure 6-6 plots temperature profiles for the AP/energetic propellant at one, two and three atmospheres during self-deflagration. The pressure increase results in an increase in surface temperature from 920 K at 1 atmosphere, to 1010 K at 3 atmospheres. The
presence of the energetic binder has clearly resulted in higher surface temperatures indicating greater extent of condensed-phase reactions.

Figure 6-6 Temperature profiles for the AP/energetic propellant at 1, 2 and 3 atmospheres during self-deflagration.

<table>
<thead>
<tr>
<th></th>
<th>101 KPa</th>
<th>202 KPa</th>
<th>303 KPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burning rate (mm/s)</td>
<td>1.75±0.15</td>
<td>2.35±0.25</td>
<td>2.9±0.25</td>
</tr>
<tr>
<td>Surface Temperature (K)</td>
<td>920±80</td>
<td>980±80</td>
<td>1010±80</td>
</tr>
<tr>
<td>n</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>nTs</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table 6-4 Burn rate and surface temperature data for AP/energetic binder propellants at one, two and three atmosphere.
Table 6-4 lists the burning rate, surface temperature and pressure and surface temperature exponents for the AP/energetic binder propellant. The pressure exponent in the burning rate equation is slightly higher than MURI 4, while the pressure exponent in the surface temperature equation is slightly lower. Since the burn rate and surface temperature data were collected over a small range of pressures, even small variations in burning rate and surface temperature can result in large changes in the exponents. Hence it is ill advised to suggest physical or chemical effects of the binder on the small differences in exponents between the AP/energetic binder and MURI 4.

6.1.1.3 AP and AP+AN/HTPE Propellants

The AP and AP+AN/HTPE propellants are the third set of AP based propellants tested in this study. In addition to the oxidizer, this propellant contains an energetic plasticizer and binder. The AP+AN propellants have two different compositions resulting in an AP+AN low rate propellant and an AP+AN high rate propellant. Table 6-5 lists the burning rates and surface temperatures for the three propellants at one atmosphere. Comparisons with table 6-3 and 6-1 show that the AP/HTPE propellant (1025K ) has surface temperatures that are significantly higher than the AP/energetic (955 K) and the MURI 4 (750 K) propellants. These higher surface temperatures are due to the energetic plasticizer and binder in the AP/HTPE propellants undergoing larger amounts of condensed-phase exothermic reactions. The surface temperature measurements for these propellants also had the largest uncertainties due to the
heterogeneous and multi-dimensional nature of the propellant surface. The effect of laser flux on the surface temperature could not be established due to the large uncertainties in surface temperature measurement. Parr and Hanson-Parr measured self-deflagration surface temperatures for these propellants to be 1100, 812 and 1050 K [82]. Clearly within the standard deviations of these measurements, the temperatures in Table 1 appear to be consistent with the measurements of Parr and Hanson-Parr.

<table>
<thead>
<tr>
<th>Propellant Type</th>
<th>60 W/cm² Burn Rate</th>
<th>35 W/cm² Burn Rate</th>
<th>Surface Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP</td>
<td>1.75±0.15 mm/sec</td>
<td>1.5±0.15 mm/sec</td>
<td>1025 ±150 K</td>
</tr>
<tr>
<td>AP+AN high rate</td>
<td>1.70±0.15 mm/sec</td>
<td>1.55±0.15 mm/sec</td>
<td>1000 ±150 K</td>
</tr>
<tr>
<td>AP+AN low rate</td>
<td>1.35±0.1 mm/sec</td>
<td>1.1±0.1 mm/sec</td>
<td>900 ±100 K</td>
</tr>
</tbody>
</table>

Table 6-5 Burn rate and surface temperature measurements at one atmosphere at mean laser fluxes of 35 and 60 W/cm² for the HTPE propellants

The uncertainties in the surface temperature measurements are highest for these propellants. A lack of sub-surface interaction between the AP particles and the HTPE binder, or the presence of large AP particles could result in large surface irregularities and multi-dimensional combustion processes and hence, larger uncertainties in the surface temperature measurement. Since the particle size information is not available to the author, this postulate was not further evaluated. Since the propellant surfaces are assumed to be one-dimensional in experimental, theoretical and numerical analyses, these multi-dimensional phenomena were not studied in any detail.

Table 6-6 lists the surface temperature and burning rates for the three propellants at one, two and three atmospheres. The surface temperatures listed at two and three
atmospheres were obtained during self-deflagration, while the temperature listed at one atmosphere was obtained at a laser flux of 35 W/cm². Due to the larger uncertainties in these measurements, the surface temperature at 1 atmosphere and a laser flux of 35 W/cm² is assumed to be equal to the surface temperature during self-deflagration.

<table>
<thead>
<tr>
<th>Propellant Type</th>
<th>101 KPa</th>
<th>202 KPa</th>
<th>303 KPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>Tₛ (K)</td>
<td>rₛ (mm/s)</td>
</tr>
<tr>
<td>AP</td>
<td>0.42</td>
<td>1025</td>
<td>1.4</td>
</tr>
<tr>
<td>AP+AN high rate</td>
<td>0.4</td>
<td>1000</td>
<td>1.4</td>
</tr>
<tr>
<td>AP+AN low rate</td>
<td>0.45</td>
<td>900</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 6-6 Burn rate and surface temperature measurements for the HTPE propellants at one, two and three atmospheres.

Due to the large uncertainties in the surface temperature measurements, the three propellants can be considered to have nearly constant temperatures with the increase in pressure. The burning rate exponents for the AP/HTPE, the AP+AN high rate and AP+AN low rate propellants are 0.42, 0.4 and 0.45 respectively. The burning rate pressure exponents are very similar to the MURI propellants and the AP/energetic propellant. The surface temperature exponent was not obtained due to an insufficient number of data points.

6.1.2 Steady-State Analytical Analysis

The objective of this analysis is to estimate the heat release as a function of the incident laser heat flux in the surface reaction zone. The process is assumed to be quasi-steady because the characteristic time for this heat release layer is very small compared to
that of the warm-up zone (preheated zone). Since the analysis has been described in section 5.1.3, only the final form of the heat conduction will be presented.

To evaluate the condensed phase reaction zone heat release, the equation can be written as

\[
H = C_c T_s - C_c T_o - \frac{q_f}{\rho r_b} - \frac{q_r}{\rho r_b} = C_c (T_s - T_o) - \frac{1}{\rho r_b} (q_f + q_r)
\]  

(6.3)

where a positive value of \( H \) denotes exothermic heat release.

Since the AP particles undergo a phase-change in the condensed-phase from an ortho-rhombic to a cubic structure, the heat of phase transformation can be included into equation 6.3 resulting in

\[
H = C_c T_s - C_c T_o - \frac{q_f}{\rho r_b} - \frac{q_r}{\rho r_b} + q^* = C_c (T_s - T_o) - \frac{1}{\rho r_b} (q_f + q_r) + q^*
\]  

(6.4)

where \( q^* \) has a value of 14-15 cal/gm.

Since the three sets of propellants are primarily AP composite propellants, the condensed-phase specific heat and density are assumed to be 0.35 cal/gm and 1.6 gm/cc respectively.

### 6.1.2.1 MURI 4 and 5 Propellants

Table 6-7 lists the heat release in the surface reaction zone for MURI 4 at 1, 2 and 3 atmospheres. Since the temperature profiles were assumed to be similar for MURI 4 and 5, and the measured burning rates for MURI 4 and 5 are also similar, the heat releases should be identical and were not studied here. Zenin estimates the absorption co-efficient
of the radiant flux at the propellant surface to be 0.4 [101]. To estimate the laser flux on
the surface, the transmissivity of the plume is assumed to be 1 with the surface reaction
zone absorbing 40\% of the laser heat flux. Zenin also recorded the radiant fluxes from
the combustion plume that are incident towards the propellant surface through the use of
light micro-calorimeters. He estimated the radiant fluxes to be 0.8 – 1 \% of the energy
released in the condensed-phase reaction zone. Hence the radiant effects are neglected in
the heat release parameters listed in table 6-7.

<table>
<thead>
<tr>
<th>Heat Flux (W/cm²)</th>
<th>1 atmosphere</th>
<th>2 atmospheres</th>
<th>3 atmospheres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Release (cal/gm)</td>
<td>113</td>
<td>120</td>
<td>125</td>
</tr>
<tr>
<td>T_s (K)</td>
<td>720</td>
<td>750</td>
<td>775</td>
</tr>
</tbody>
</table>

Table 6-7 Pressure and laser flux effects on heat release in the surface reaction zone for
MURI 4.

The table shows that the heat release in the surface reaction zone increases with an
increase in laser flux or pressure albeit by a small amount. At one atmosphere, the heat
release increases from 113 cal/gm during self-deflagration to 125 cal/gm during laser-
assisted combustion at 60 W/cm². During self-deflagration, the heat release increases
from 113 cal/gm at 1 atmosphere, to 135 cal/gm at 3 atmospheres. Zenin estimates the
heat release for an AP/HTPB propellant to be 130 cal/gm at 5 atmospheres [101]. Clearly
the values obtained in this study agree quite well with his findings.
6.1.2.2 AP/Energetic Binder Propellant

The surface absorptivity of the AP/energetic propellants is assumed to be equal to that of the AP/HTPB propellants and is set to 0.4. Video images do not show any noticeable differences in the gas-phase combustion behavior between the AP/HTPB and AP/energetic binder propellants. Hence the transmissivity is assumed to be 1. The thermal diffusivities and thermal conductivities of these propellants are also assumed to be similar to the AP/HTPB propellants. Hence the differences in the surface heat release term for these two classes of propellants will be due to differences in the surface temperature and differences in the gas-phase heat feedback.

Table 6-8 lists the surface temperatures and heat release values for the AP/energetic propellant at 1, 2 and 3 atmospheres during self-deflagration, and surface temperatures and heat release values at laser-fluxes of 35 and 60 W/cm² at 1 atmosphere. The surface heat release also increases with an increase in laser flux or pressure. At 1 atmosphere, the heat release increases from 160 cal/gm during self-deflagration, to 177 cal/gm during laser-assisted combustion at 60 W/cm². During self-deflagration, the heat release increases from 160 cal/gm at 1 atmosphere, to 205 cal/gm at 3 atmospheres.
These trends are consistent with the AP/HTPB propellants. However, the AP/energetic propellant produces heat release values that are significantly larger than the AP/HTPB propellant. This is consistent with the hypothesis that the energetic binders undergo larger amounts of exothermic reactions in the condensed-phase when compared to the relatively inert HTPB.

### 6.1.2.3 AP and AP+AN/HTPE Propellants

Since the compositions of these propellants are unknown to the author, the thermal and optical properties are assumed to be equal to the published properties for typical AP/HTPB propellants. Hence the only differences in the heat release values for the three classes of propellants are due to differences in surface temperature and gas-phase heat feedback.

Table 6-9 lists the surface temperature and heat release for the three HTPE based propellants at one, two and three atmospheres during self-deflagration. The results clearly show that for all three propellants, the increase in pressure results in an increase in...
the exothermic heat release in the surface reaction zone. Due to the large uncertainties in the surface temperature measurements, these calculations were not performed as a function of the laser flux.

<table>
<thead>
<tr>
<th>Propellant Type</th>
<th>101 KPa</th>
<th>202 KPa</th>
<th>303 KPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_s (K)</td>
<td>Q_s</td>
<td>T_s (K)</td>
</tr>
<tr>
<td>AP</td>
<td>1025</td>
<td>190</td>
<td>1050</td>
</tr>
<tr>
<td>AP+AN high rate</td>
<td>1000</td>
<td>185</td>
<td>1035</td>
</tr>
<tr>
<td>AP+AN low rate</td>
<td>900</td>
<td>155</td>
<td>930</td>
</tr>
</tbody>
</table>

Table 6-9 Effect of pressure on heat release in the surface reaction zone for the AP and AP+AN/HTPE propellants.

The increase in pressure results in an increase in the surface reaction zone heat release for all three classes of propellants. The different binders in the three classes of propellants results in a different heat release values, different surface temperatures and burning rates. Despite the different binders, the three classes of propellants show similar trends in heat release, surface temperature and burning rate changes to changes in pressure or laser flux.

6.1.3 Steady-State Modeling Analysis

The object of this analysis was to use the CHEMKIN code to verify the effects of heat flux on gas-phase temperature profiles and gas-phase heat feedback. It is argued that the AP/HTPB propellant can be modeled as a one-dimensional flame if the AP particle sizes are small and the pressures are low [97]. Since the species measurements were
performed at one atmosphere, the particle size effect is assumed to be small. The outputs from this mechanism showed very good agreement with the species profiles of Korobeinichev et al [95,96]. This mechanism was also verified by testing the output of the mechanism against experimental measurements.

Figure 6-7 compares modeling predictions versus measured species profiles at one atmosphere at a laser flux of 35 W/cm². The figure shows that the experimental and numerical profiles for CO₂, HCN, HCL and H₂O with the experimental data presented in closed symbols and the numerical data in open symbols. The figure shows that there is reasonable agreement between the experimental and modeling data. The experimental data shows substantial scatter due to the high temperature gradients and harsh combustion environments associated with the AP/HTPB propellants. The variation in the sensitivity coefficients of the measured species lead to an uncertainty of about 10% in the measured species profiles. The experimental mole fractions are higher than the modeling results for these four major species because some species like HCLO₄ that are present near the combustion surface are not detected experimentally. Hence the normalized mole fractions for the detected species are higher than the modeling results. The figure clearly suggests that the gas-phase mechanism is quite predictive under these test conditions.
Figure 6-7 Comparison of experimental data (closed symbols) and model results (open symbols) at a laser flux of 35 W/cm².
Figure 6-8 plots the predicted effect of propellant burning rate on gas-phase temperature profiles at 101 KPa (1 atmosphere). The plots were created using the temperature profiles along with surface and gas-phase species profiles as input parameters. To obtain these profiles the energy equation was solved in the CHEMKIN code. The effect of heat flux was accounted for via experimental burning rates (mass flux) and surface temperature.

Burning rates of 1.3 and 1.8 mm/s were used to simulate self-deflagration and laser-assisted combustion at 60 W/cm² for the MURI propellants. The figure clearly shows
that the gas-phase heat feedback decreases with an increase in burning rate. The decrease in gas-phase heat feedback with burning rate is not as distinct as HMX and hence could not be quantified through experimental observations. The temperature gradient driving the gas-phase heat feedback (computed through modeling data) decreases from $2.7 \times 10^4$ K/cm to $2.1 \times 10^4$ K/cm with the increase in burning rate. Hence the gas-phase heat feedback decreases with an increase in the laser flux though the effect of the laser flux on the gas-phase heat feedback is significantly smaller when compared to HMX.

The experimentally measured gas-phase heat feedback was about $4 \times 10^4$ K/cm for the MURI propellants, while the modeling efforts predict a flux of $2.7 \times 10^4$ K/cm. Clearly the experimental and modeling results are in reasonable agreement and suggests that the two could be used in tandem to explore effects of heat release and heat feedback on the unsteady laser and pressure-driven response amplitudes.

6.2 Laser-Driven Combustion

6.2.1 MURI 4 and 5

The MURI 4 and 5 propellants had higher burning rates when compared to HMX. As discussed in chapter 3, the higher consumption rates lead to larger errors in amplitude and phase response. Hence laser-driven response measurements were limited to mean laser fluxes of 35 and 60 W/cm$^2$. To ensure one-dimensional thrust response data, the propellant samples were placed in a quartz vial that was 3/8” in diameter. The propellants were cut into the required size and glued into the vial to prevent them from
dislodging during combustion. Tests were performed at atmospheric pressure in air at heat fluxes of $35\pm15$ and $60\pm15$ W/cm$^2$, with driving frequencies ranging from 3.9 to 250 Hz. Initial characterization of the propellant sample was performed by using a single driving frequency during each test. Once the propellants burn rate and behavior were understood, sweeps with discrete increments of frequency were used. The thrust signals beyond 250 Hz were not considered due to the unacceptable noise to signal ratio.

Figure 6-9 shows the amplitude and phase response for MURI#4 propellants at mean heat fluxes of 35 and 60 W/cm$^2$. The MURI propellants also needed a minimum oscillatory heat flux of $\pm15$ W/cm$^2$ to obtain a clear thrust response.

Figure 6-9(a) shows a low thrust response at low frequency, a rise to maximum, and then decay at the higher frequencies. Even though the propellant is heterogeneous, the thrust response shows a trend consistent with the QSHOD framework. An increase in the mean heat flux tends to decrease the dimensional thrust response amplitude. At 35 and 60 W/cm$^2$, the maximum amplitudes are $1.8 \times 10^{-5}$ N/W and $1.7 \times 10^{-5}$ N/W, respectively. The maximum amplitudes are measured at 16 and 24 Hz for the incident laser heat fluxes of 35 and 60 W/cm$^2$ respectively. The amplitude shows a shift to a higher dimensional frequency with an increase in heat flux. This is also due to the higher burning rate (shorter thermal relaxation) associated with the increased heat flux.

Figure 6-8(b) shows the phase response for MURI#4. At 35 W/cm$^2$, the phase shows a monotonic drop from a lead of 8 degrees at 4 Hz to a lag of about 30 degrees at 250 Hz. At 60 W/cm$^2$, the phase shows also shows a monotonic drop from a lead of 12 degrees at 4 Hz, to a lag of about 35 degrees at 250 Hz. At 35 W/cm$^2$, the relative phase is zero at 16 Hz, while at 60 W/cm$^2$; it is zero at 24 Hz. These zero phase values occur at
the same dimensional frequency as the maximum amplitude response and show consistency in the experimental results.

Figure 6-10 shows the amplitude and phase response for MURI#5. This propellant is very similar in its composition to MURI#4 and exhibits similar response characteristics. Figure 6-10 (a) shows the amplitude response for MURI#5 at heat fluxes of 35 and 60 W/cm². The thrust response also shows a trend consistent with the QSHOD framework. An increase in the mean heat flux tends to decrease the dimensional thrust response amplitude. At 35 and 60 W/cm², the maximum amplitudes are 1.85 \times 10^{-5} \text{ N/W} and 1.65 \times 10^{-5} \text{ N/W}, respectively. The maximum amplitudes are measured at 16 and 24 Hz. for the incident laser heat fluxes of 35 and 60 W/cm² respectively and also show a shift to a higher dimensional frequency with an increase in heat flux.

Figure 6-10 (b) shows the phase information for MURI#5 at one atmosphere in air. The phase shows leads of 10 and 15 degrees at 4 Hz for incident laser heat fluxes of 35 and 60 W/cm². The phase is zero at 16 Hz for an incident heat flux of 35 W/cm², and is zero at 24 Hz for a heat flux of 60 W/cm². At 250 Hz, the phase is 25 and 30 degrees behind the driving signal at laser fluxes of 35 and 60 W/cm² respectively.
Figures 6-9 MURI#4 thrust amplitude and phase response at heat fluxes of 35±15 and 60±15 W/cm²
Figures 6-10 MURI#5 thrust amplitude and phase response at heat fluxes of 35±15 and 60±15 W/cm²
Figure 6-11 is an image of MURI 4 during laser-driven combustion at 1 atmosphere at a laser flux of 35±15 W/cm². The figure clearly shows the propellant sample in the glass vial that ensures the one-dimensional response. The figure shows the flame attachment to the propellant surface. This flame is not affected by the unsteady laser flux.

To facilitate comparisons with modeling and analytical studies, the dimensional thrust response is converted to a more useful non-dimensional response through a series of experiments that helped obtain the burn rate to thrust ratio. These burn rate tests were similar in nature to tests performed for the HMX propellants. Figure 6-12 shows the
relationship between the burn rates and burn rate to thrust ratio. The burn rate was varied from 1.5 to 3 mm/sec by using incident laser heat fluxes ranging from 35 to 150 W/cm².

The physical properties of the MURI propellants are restricted information. So the thermal diffusivity was assumed to be 0.016 cm²/sec. This is a typical value for a heterogeneous AP/HTPB propellant.

Figure 6-13 shows the non-dimensional amplitude response for MURI#4 at 35 and 60 W/cm². The maximum amplitude of the non-dimensional response for MURI#4 at 60 W/cm² is 0.76, while that at 35 W/cm² is 0.87. For HMX the increase in heat flux from 35 to 60 W/cm² did not affect the response, but for this propellant there is a clear decrease in the response.

Figure 6-12 Relation between burning rate and burning rate to thrust ratio for MURI#4 and MURI#5
Figure 6-13: Thrust Response Amplitude for MURI#4 versus non-dimensional frequency.

Figure 6-14: Thrust Response Amplitude for MURI#5 versus non-dimensional frequency.
Figure 6-14 shows the thrust response amplitude for MURI#5 at 35 and 60 W/cm². The maximum amplitude for MURI#5 at 60 W/cm² is 0.81, while that at 35 W/cm² is 0.85. This propellant behavior is consistent in trend with MURI#4, but the drop-off in amplitude response with heat flux is smaller.

For HMX, the laser-driven experiments were primarily condensed-phase responses to the laser flux, while the laser-driven experiments with the MURI propellants are condensed-phase responses to both the laser and the gas-phase heat feedback. With an absorptivity of 0.4, the mean laser fluxes of 35 and 60 W/cm², translate to 14 and 24 W/cm² respectively. Hence the laser is being modulated at 14±6 and 24±6 W/cm². The steady-state temperature gradients are 2.7 and 2.1 x 10⁴ K/cm and the thermal conductivity is 1.75 x 10⁻⁴ cal/cm-K, giving gas-phase heat feedbacks of 19 and 15 W/cm² at the two laser fluxes. The unsteady components of the gas-phase heat feedback are obtained by running Chemkin. The burning rates at the maximum and minimum values of the unsteady laser fluxes and estimated temperature profiles for the mean laser fluxes are used and the energy equation is solved. This is best illustrated through the following steps:

a) Use tables 6-1 and 6-2 to relate the steady-state burning rate data to mean laser flux.

b) Obtain burning rate values for the maximum and minimum values of the laser flux. (r_b at 20 and 50 W/cm² for a laser flux of 35±15 W/cm²).

c) Solve the energy equation through Chemkin using this burning rate at 1 atmosphere and obtain temperature profiles and gas-phase heat feedback.
Table 6-10 Total heat flux as a function of unsteady laser-flux during laser-driven combustion.

<table>
<thead>
<tr>
<th>Unsteady laser flux (W/cm²)</th>
<th>Surface Laser flux (W/cm²)</th>
<th>heat feedback (W/cm²)</th>
<th>Total heat flux (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35±15</td>
<td>14±6</td>
<td>19±1.8</td>
<td>33±4.2</td>
</tr>
<tr>
<td>60±15</td>
<td>24±6</td>
<td>15±2.1</td>
<td>39±3.9</td>
</tr>
</tbody>
</table>

The table shows the unsteady component of the heat feedback increases with laser flux. This is the opposite trend compared to HMX where the unsteady component of the heat feedback decreases with an increase in laser flux. The table also shows that the total heat flux has a larger mean value but a lower unsteady component at the higher laser flux. Since the sum of the unsteady components of the laser flux and heat feedback decreases with an increase in laser flux, the response amplitudes also decrease with an increase in laser flux.

6.2.2 AP/Energetic Propellant

Thrust response measurements were made at incident laser heat fluxes of 35±15, and 60±15 W/cm² at frequencies ranging from 4 to 250 Hz under laser-driven combustion. Figure 6-15 shows the resulting thrust amplitude and phase response. Like HMX and the MURI 4 and 5 experiments, oscillatory heat fluxes below ±15 W/cm² did not give a clear thrust response.

The thrust amplitude appears to be relatively constant at low frequency and then decreases with an increase in frequency. This is in sharp contrast to the response profiles observed for the MURI 4 and 5 propellants that showed a clear maximum amplitude
response at ‘resonant’ frequency’. Figure 6-15 (a) shows that an increase in the mean heat flux decreases the maximum response amplitude. This trend has also been observed in our previous studies [84] and in the work of Zarko et al [55,56]. At a mean heat flux of 35 W/cm², the maximum thrust amplitude was 0.02 mN/W. This maximum amplitude was observed at driving frequencies of 4 to 64 Hz. Further increases in the driving frequency resulted in lower values for the response amplitude. At 250 Hz, the response amplitude was 0.013 mN/W. At a mean incident laser heat flux of 60 W/cm², the maximum thrust response of 0.013 mN/W and was measured at frequencies up till 64 Hz. An increase in the driving frequency beyond 64 Hz decreases the response amplitude monotonically. At 250 Hz, the response amplitude was 0.0095 mN/W. The change in heat flux does not show a frequency shift of the maximum amplitude response.

Figure 6-15 (b) shows the relative phase signal as a function of frequency and heat flux. The phase signal shows an in-phase response at low frequency that decreases monotonically to a lag with an increase in frequency. For an incident heat flux of 35 W/cm², the phase signal shows an in-phase response at 4 Hz, which remains constant till about 30 Hz. The phase then drops to a lag of 35 degrees at 250 Hz. The higher heat flux shows a phase of zero for frequencies ranging from 4 to 30 Hz and then decays to a lag of 26 degrees at 250 Hz. The phase response appears to be constant and in-phase at low frequency. The amplitude response is constant and maximum at low frequency and shows consistency in the response amplitude and phase measurements.
Figure 6-15 Thrust Response for the AP/energetic propellant at 35 and 60 W/cm$^2$
Figure 6-16 is a plot of the relationship between burning rate and the ratio of burn rate to measured thrust. At incident laser heat fluxes of 35 and 60 W/cm², the burn rates were 2.05 and 2.30 mm/s, and the corresponding burn rate to thrust ratios were 4800 and 4300 mm/s/Newton respectively.
Figure 6-17 Thrust Response Amplitude versus $\Omega$ for the AP/energetic propellant

Figure 6-17 plots the non-dimensional thrust response amplitudes for the AP/energetic propellant as a function of $\Omega$. The figure shows that at both laser fluxes, the response amplitudes are 0.7 at low frequency and then decrease with a further increase in frequency. The response amplitudes decrease with frequency increases beyond an $\Omega$ value of 15. Comparisons with the MURI 4 and 5 data plotted in figures 6-13 and 6-14 reveal two distinct differences.

a) The increase in laser flux does not decrease the response amplitude

b) The response amplitude is nearly constant at low frequency.
The experimental temperature profiles measure near-surface temperature gradients of $1 \times 10^5 \, \text{C/cm}$. The thermal conductivity is assumed to be $1.75 \times 10^{-4} \, \text{cal/cm-C}$, resulting in gas-phase heat feedbacks that are approximately $73 \, \text{W/cm}^2$ at both laser fluxes. Due to the unknown composition of the binder material, Chemkin calculations to estimate the gas-phase heat feedback were not performed. Assuming an absorptivity of 0.4 results in incident laser fluxes of 14 and 24 W/cm$^2$. The steady-state gas-phase heat feedback is larger than the laser flux and does not change with the increase in laser flux. Hence the unsteady component of the gas-phase heat feedback is assumed to be constant with laser flux. The total mean components of the flux incident on the propellant surface are 87 and 97 W/cm$^2$ at the two laser fluxes. If the unsteady components of the heat feedback are unaffected by the increase in laser flux, the unsteady components of the total flux are constant at both laser fluxes. The propellant condensed-phase produces nearly constant response amplitudes at the two laser fluxes due to the nearly constant response amplitudes.

It is possible that the unsteady gas-phase heat feedback for the AP/energetic binder propellant increases with laser flux like the MURI 4 and 5 propellants. The AP/energetic propellants have a gas-phase heat feedback that is 5 times greater than the MURI propellants and hence should have unsteady components of the heat feedback that are greater than the unsteady component of the laser flux. This could result in larger unsteady components of the total flux at the higher mean laser fluxes and hence should result in higher response amplitudes. However the increase in surface temperature results in greater amount of exothermic reactions in the condensed-phase and hence reduces the effect of dynamic changes in the gas-phase condensed-phase interface. Hence the
increase in the unsteady laser flux could possibly mask the effect of the increase in exothermic reactions in the condensed-phase resulting in similar response amplitudes at both mean laser fluxes.

In order to understand the nearly constant response amplitudes at low driving frequency, the surface heat release is evaluated. Table 6-4 shows that the surface temperature for the AP/energetic propellant is significantly higher than the MURI propellants (table 6-1) at similar test conditions and suggest larger amounts of exothermic reactions in the condensed-phase. Large amounts of exothermic reactions would result in a condensed-phase that is insensitive to variations in the dynamic phenomena at the surface/gas-phase interface and hence yield nearly constant response amplitudes at low frequency.

6.2.3 AP and AP+AN/HTPE Propellants

The laser-driven response measurements for these three propellants were made at incident laser heat fluxes of 35±15 and 60±15 W/cm² at frequencies ranging from 4 to 250 Hz. Figure 6-16 shows the resulting thrust amplitude and phase response at 35 W/cm². Once again a 95% confidence interval based on multiple experiments performed at each condition was used to calculate the random error.

The thrust amplitude appears to be relatively constant at low frequency and then decreases with an increase in frequency for both AP+AN propellants. The flat response for the AP+AN propellants could be due to either a larger amount of sub-surface reactions or differences in condensed-phase response between the AP and AN in the
AP+AN/HTPE propellants. Previous figures have shown that these propellants exhibit surface temperatures that are much higher than those measured for AP/HTPB propellants ($T_s = 750$ K). This would suggest that the relatively flat response profile at low frequency could be due to larger amount of exothermic reactions in the condensed-phase. The AP propellant also appears to show relatively constant response amplitudes at low frequency that decreases with a further increase in frequency. The surface temperature for the AP propellant is the highest of the three propellants used in this study and would suggest that the AP propellant undergoes the largest amount of exothermic reactions in the condensed-phase. Table 6-7, 6-8 and 6-9 show that the AP/HTPE propellants have the highest exothermic heat release in the condensed-phase. Hence the relatively constant response amplitudes at low frequency are probably due to exothermic reactions in the condensed-phase. This is in sharp contrast to the response profiles observed for the MURI 4 and 5 propellants that showed a clear maximum amplitude response at ‘resonant’ frequency.

Figure 6-18(a) shows that the maximum thrust amplitude for the AP based propellant was 0.011 mN/W at frequencies ranging from 4 to 24 Hz. The maximum response amplitudes for the AP+AN low rate and high rate propellants was 0.01 and 0.08 mN/W at driving frequencies ranging from 4 to 24 Hz. Further increase in the driving frequency resulted in lower values for the response amplitude. Hence there is a “threshold” frequency for the propellants beyond which the response amplitude decreases. The response amplitude for the AP based propellant decreased from 0.011 mN/W at 24 Hz to 0.007 mN/W at 125, while the response amplitudes for the AP+AN low and high rate
propellants decrease from 0.008 and 0.01 mN/W at 24 Hz, to 0.005 mN/W at 250 and 125 Hz respectively.

Figure 6-18(b) shows the relative phase at 35 W/cm² for the three propellants. For all three propellants, the relative phase is zero at low frequency and decreases to a lag of about 50 degrees with an increase in frequency.

Figure 6-19 plots the laser-driven response amplitude and relative phase for the AP and AP+AN propellants at a laser flux of 60 W/cm². The response amplitudes are similar to those observed at the laser flux of 35 W/cm². The AP and the AP+AN based propellants have a flat response at the low frequency, which drops off with an increase in frequency. The response amplitudes for the three propellants are similar to the amplitudes at a laser flux of 35 W/cm². The AP and the AP+AN low rate propellant responses fall off in amplitude above 24 Hz, while the AP+AN high rate propellant response falls off in response amplitude above 32 Hz. With an increase in the laser flux, the threshold frequency increases for the AP+AN high rate propellant, but remains constant for the AP and the AP+AN low-rate propellant. This absence of a shift in threshold frequency for the AP and the AP+AN low rate propellant could be due to the fact that testing is performed at discrete frequencies and the frequency associated with the condensed-phase thermal relaxation time lies between the two test frequencies. The increase in frequency with laser flux is characteristic of the condensed-phase thermal relaxation effect and was documented in section 6.2.1. In the previous sub-sections, the dimensional thrust response of the AP/energetic binder as well as the MURI 4 and 5 propellants decreased with an increase in laser flux, while the response for these propellants remain largely unaffected by laser flux. Clearly the presence of the HTPE
binder appears to have altered the propellant response to mean heat flux. A detailed investigation of the physical and chemical variations between the binders under laser heating may help explain these differences in behavior.

Figure 6-20 plots the burning rate to thrust ratio as a function of burning rate for the three HTPE propellants. The AP/AN high rate and AP/HTPE propellants have similar burning rate and very similar burning rate to thrust ratios. The AP/AN low rate propellant has a lower burning rate and has burning rate to thrust ratios that range from 4100 to 2900 at burning rates of 0.95 and 1.50 mm/s respectively. These burning rate to thrust ratios are used to obtain the non-dimensional laser-driven response amplitude.
Figure 6-18 Thrust Response for laser-driven combustion in air at 35±15 W/cm² for the HTPE propellants.
Figure 6-19 Thrust Response for laser-driven combustion in air at $60\pm 15$ W/cm$^2$ for the HTPE propellants.
Figure 6-20 Relationship between burning rate and burning rate to thrust ratio for the HTPE propellants

Figure 6-21 (a) and (b) plot the non-dimensional laser-driven response amplitudes at 35±15 and 60±15 W/cm². For the AP/HTPE propellant, the maximum response amplitude increases from 0.4 to 0.6 with an increase in laser flux from 35 to 60 W/cm². The AP+AN high rate propellant response increases from 0.40 to 0.55 with the increase in laser flux, while the AP+AN low rate propellant increases in response from 0.35 to 0.45 with the increase in laser flux. The propellants have nearly constant response amplitude at low frequency that decreases beyond with an increase in frequency beyond the threshold frequency.
Figure 6-21 Non-Dimensional Response Amplitudes at 35±15 (a) and 60±15 (b) W/cm²
Like the AP/energetic binder propellants, these three propellants have high surface temperatures and hence larger amounts of exothermic reactions in the condensed-phase compared to the AP/HTPB propellants. The surface temperature measurements and the response amplitudes validate the hypothesis that larger amounts of exothermic reactions result in a condensed-phase that is insensitive to variations in the dynamic phenomena at the surface/gas-phase interface. Hence the response amplitudes are nearly constant at low frequency.

These figures show an unusual trend. With the increase in laser flux, there is an increase in the non-dimensional laser-driven response amplitudes. Previous sections have shown that the response amplitude for the AP/energetic and the MURI 4 and 5 propellants stay constant or decrease with an increase in laser flux. To understand this anomalous behavior of the response amplitudes for the three propellants, with the increase in laser flux, the gas-phase heat feedbacks are evaluated. The gas-phase temperature gradients are $1.3 \times 10^5 \text{ C/cm}$ and have a thermal conductivity of $1.75 \times 10^{-4} \text{ cal/cm C}$ resulting in gas-phase heat feedbacks of $95 \text{ W/cm}^2$. The large surface temperature variations make it difficult to predict the variation in surface temperature and gas-phase heat feedback with an increase in laser flux. The modeling results have shown that the unsteady component of the gas-phase heat feedback increases with laser flux for the MURI propellants. This may also be true for this set of propellants and is discussed in the next paragraph.

The HTPE based propellants have the largest surface temperature gradients and hence the largest gas-phase heat feedback. For the MURI propellants, the unsteady component of the gas–phase heat feedback was smaller than the unsteady component of
the laser flux and hence resulted in a smaller unsteady component of the net flux incident on the propellant surface. This resulted in nearly constant response amplitudes with the increase in laser flux. The gas-phase heat feedbacks for the HTPE propellants are 5 times larger than the MURI 4 and 5 propellants. Hence the unsteady components of the heat feedback may also be larger than the unsteady components of the laser flux. An increase in the unsteady component of the gas-phase heat feedback with an increase in the mean laser flux would result in an increase in the unsteady component of the total flux incident on the propellant surface. This could result in the larger response amplitudes at the higher mean laser flux. For the AP/energetic propellant, the unsteady gas-phase heat feedback may be similar in magnitude to the unsteady laser flux. Hence a small change in the unsteady gas-phase heat feedback may be masked by the experimental uncertainty in the response amplitude data.

6.3 Pressure-Driven Combustion

6.3.1 MURI 4 and 5

MURI#4 and 5 propellants were cut into cylindrical pellets, 0.375” in diameter and 0.25” in height. The propellant samples were also placed in a quartz vial during response measurements to obtain one-dimensional thrust response. Tests were performed at an initial pressure of one, two and three atmospheres with air as the ambient gas during self-deflagration and at mean laser fluxes of 35 and 60 W/cm². The driving frequencies ranged from 4 to 96 Hz. During thrust response tests, the ambient pressure rose from
one to about two atmospheres due to the small chamber volume. Compressed air was used to provide ambient pressures of two and three atmospheres. The KCl window on the top of the chamber would rupture at pressures above three atmospheres and lead to depressurization. Hence initial chamber pressures were limited to an upper limit of three atmospheres.

Figure 6-22 shows the thrust response amplitude and phase for MURI#4 during pressure-driven combustion at one atmosphere. Figure 6-22 (a) shows the amplitude responses decrease with an increase in heat flux. The maximum amplitude decreases from 1.35 x 10^{-3} N/atm to 1.1 x 10^{-3} N/atm with an increase in heat flux from 35 to 60 W/cm^2. The maximum amplitude shifts from 16 to 24 Hz with an increase in heat flux. This shift in resonance frequency with an increase in heat flux is believed to be due to the condensed phase thermal relaxation.

Figure 6-22 (b) shows the phase response for MURI#4. The phase shows a lead of about 20 degrees at 4 Hz, and decreases to a lag of about 23 degrees at 96 Hz for a heat flux of 35 W/cm^2. The phase is zero at 16 Hz. For an incident heat flux of 60 W/cm^2, the phase shows a lead of 25 degrees at 4 Hz, and a lag of 28 degrees at 96 Hz. The phase is zero at 24 Hz. The phase is expected to be zero at resonant frequency. In these experiments, the phase is zero at the frequency where the amplitude is the maximum for both laser flux conditions. This clearly shows consistency in the measurement of both amplitude and phase.

Figure 6-23 shows the amplitude and phase response for MURI#5 at an initial pressure of one atmosphere. The maximum amplitude is lower for the higher heat flux.
Figure 6-22 Pressure-driven Thrust Response for MURI#4 at 1 atmosphere.
Figure 6-23 Pressure-driven Thrust Response for MURI#5 at 1 atmosphere.
The maximum amplitude decreases from $1.3 \times 10^{-3}$ to $1.1 \times 10^{-3}$ N/atm with an increase in heat flux from 35 to 60 W/cm$^2$. The maximum response amplitude also shifts in frequency from 16 to 24 Hz with an increase in heat flux. Figure 6-23 (b) shows the phase response for the propellant. At 4 Hz, the phase leads by 17 and 22 degrees for heat fluxes of 35 and 60 W/cm$^2$ respectively. The phase lags the driving signal by 20 degrees for both heat fluxes at 96 Hz. The phase is zero at 16 and 24 Hz at 35 and 60 W/cm$^2$.

![Figure 6-24](image.png)

Figure 6-24 Non-dimensional pressure-driven response amplitude versus $\Omega$ for MURI#4 and 5.

Figure 6-24 shows the non-dimensional response amplitude for MURI #4 and 5 plotted against the non-dimensional frequency. Increasing the laser flux decreases the maximum response amplitude for both propellants. The plot against $\Omega$ shows that all the maximum response values now map onto an $\Omega$ value of ~8. This is quite consistent with
the analytical and modeling results for other heterogeneous propellants [54,56]. All the maximum amplitudes lie on the same value of $\Omega$, which is a thermal relaxation parameter. Table 6-1 and figure 6-1 show that the surface temperature and the heat release in the surface reaction zone increase with an increase in laser flux, while the modeling analysis predicts that the gas-phase heat feedback decreases from 19 to 15 W/cm$^2$ with the increase in laser flux. Using an algorithm similar to the laser-driven combustion experiments, the unsteady component of the gas-phase heat feedback is evaluated. The experimentally determined pressure exponent is used to calculate the burning rate at 1.05 and 0.95 atm. The energy equation is then solved in Chemkin to obtain the gas-phase heat feedback under these conditions. Table 6-11 lists the gas-phase heat feedback at both laser fluxes and shows that the increase in laser flux decreases the steady and unsteady components of the gas-phase heat feedback. Hence the lower gas-phase heat feedbacks coupled with the increase in the exothermic reactions in the condensed-phase results in the lower response amplitudes for both MURI propellants with the increase in laser flux.

<table>
<thead>
<tr>
<th>Laser flux (W/cm$^2$)</th>
<th>Surface Laser flux (W/cm$^2$)</th>
<th>Heat feedback (W/cm$^2$)</th>
<th>Total heat flux (W/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>14</td>
<td>19±1.2</td>
<td>33±1.2</td>
</tr>
<tr>
<td>60</td>
<td>24</td>
<td>15±0.9</td>
<td>39±0.9</td>
</tr>
</tbody>
</table>

Table 6-11 Total heat fluxes as a function of the mean laser-fluxes for pressure-driven combustion of an AP/HTPB propellant.
MURI 4 and 5 propellants were tested at one, two and three atmospheres during self-deflagration. Figure 6-25 plots the response amplitudes for both propellants versus non-dimensional frequency. Three interesting observations that are consistent for both propellants

1. The response amplitudes are higher than those observed during laser-assisted combustion

The maximum response amplitudes for the MURI 4 and 5 propellants are 1.6 and 1.45 at 1 atmosphere during self-deflagration, and 1.4 and 1.3 during laser-assisted combustion at 35 W/cm². The modeling results show that the gas-phase
temperature gradient decreases from $3.1 \times 10^4$ K/cm during self-deflagrating conditions to $2.1 \times 10^4$ K/cm during laser-assisted combustion at 60 W/cm$^2$. The gas-phase heat feedback decreases from $22\pm1.4$ W/cm$^2$ during self-deflagration, to $15\pm0.9$ W/cm$^2$ during laser assisted combustion at 60 W/cm$^2$. Table 6-7 shows that the increase in laser flux increases the surface temperature and the exothermic decomposition reactions in the condensed-phase. Hence the lower response amplitudes during laser-assisted combustion are due to the smaller gas-phase heat feedback and larger amounts of exothermic reactions in the condensed-phase.

b) The response amplitudes for both propellants decrease with an increase in pressure.

The modeling results predict an increase in gas-phase heat feedback from $3 \times 10^4$ K/cm to $4.4 \times 10^4$ K/cm with an increase in pressure from one to three atmospheres. Since the steady-state gas-phase heat feedback increases from 22 W/cm$^2$ to 32 W/cm$^2$ with the increase in pressure, the unsteady components of the heat feedback also increase from $\pm1.4$ W/cm$^2$ at 1 atmosphere, to $\pm1.95$ W/cm$^2$ at 3 atmospheres. However, table 6-7 shows that the surface temperature increases from 720 to 805 K and the exothermic heat release increases from 113 cal/gm, to 135 cal/gm with the increase in pressure. Since the exothermic reactions play the role of a damping agent and the gas-phase heat feedback amplifies the response amplitude, the two mechanisms tend to negate each other. Under these conditions, the exothermic reactions in the condensed-phase appear to have a greater effect on the response amplitude and hence the lower response amplitudes at elevated pressures. For these
propellants, Culick’s model that suggests increasing condensed-phase exothermic reactions decrease the response amplitude holds true [6].

c) The response amplitude profiles become nearly constant at low frequency with an increase in ambient pressure.

The increase in pressure produces nearly constant response amplitudes for both propellants at low frequency. It is theorized that the increase in exothermic condensed-phase reactions makes the propellant less sensitive to dynamic interactions between the gas and condensed-phases and hence produces the nearly constant response amplitudes at low frequency. Table 6-7 shows that the exothermic heat release in the condensed-phase increases with pressure. Hence the nearly constant response amplitudes at low frequency are consistent with this hypothesis.
Figure 6-26 Response Amplitudes versus non-dimensional frequency for MURI 4 and 5 (flowmeter and recoil experiments).

Figure 6-26 compares the real pressure-coupled response obtained at 3 atmospheres using the recoil technique with the magnetic flowmeter data of Micci et al [66]. The flowmeter data was collected at pressures that are close to the operating pressures in rocket chambers and hence serves as a useful link to facilitate a comparison between low-pressure recoil measurements and the realistic phenomena within a rocket combustion chamber.

The recoil data detects lower response values for the MURI 4 and 5 propellants compared to the flowmeter data. However this cannot be used to interpret the capabilities of one technique versus the other because the MURI propellants are known to exhibit peculiar burning rate profiles at elevated pressures. It is also possible that different
driving mechanisms come into play at higher pressure. Since the recoil experiments cannot be conducted at the high test pressures associated with rocket chambers, it is difficult to compare the effect of response amplitudes or the real part of the response between the two experiments and is a drawback associated with these recoil experiments. The recoil experiments allow an evaluation of the effects of the different driving mechanisms on response amplitudes and hence is a useful tool to understand combustion instability.

For both types of experiments, the peak response occurs at an $\Omega$ value of 10-15. It is believed that this peak is associated with the condensed-phase thermal relaxation and is consistent in both experiments. Hence it is interesting to note that both experiments are detecting the condensed-phase response to a pressure-variation and predict similar values of $\Omega$ for the peak response.

Figure 6-27 plots the effect of exothermic reactions in the condensed-phase based on Culick’s analytical expression for the pressure-coupled response [6]. The figure plots the real response function as a function of non-dimensional frequency. The curves were plotted for Q values of 0.3 and 1 that correspond to heat release numbers of 47 and 155 cal/gm respectively. The figure clearly shows that an increase in the exothermicity in the condensed-phase, results in lower response functions. It should be noted that this model does not provide predictive numbers for AP/HTPB propellant response. This could be due to the simplifying assumptions used to obtain the analytical solution. However this model serves as a useful tool to understand the qualitative effects of physical phenomena on the behavior of the response functions.
6.3.2 AP/Energetic Propellants

The AP/energetic propellants were also cut into cylindrical pellets, 0.375” in diameter and 0.25” in height and placed in a quartz vial during response measurements to obtain one-dimensional thrust response. Thrust response measurements during pressure-driven combustion have been made during self-deflagration and laser-assisted combustion at 35 and 60 W/cm² at frequencies of 4 to 96 Hz. Each thrust response measurement was carried out at a single driving frequency.
Figure 6-28 shows the non-dimensional thrust amplitude and phase response at 35 and 60 W/cm² during pressure-driven combustion. The figure shows that the amplitude response remains almost constant at low frequency and drops off with an increase in driving frequency beyond a threshold frequency. At 35 W/cm², the maximum amplitude showed a decrease from 1.05 at 48 Hz to a value of 0.74 at 96 Hz. At 60 W/cm², the amplitude response was also constant at low frequency and decreased from its maximum value of 0.87 at 48 Hz, to 0.71 at 96 Hz. The increase in the laser flux decreased the maximum response amplitude. Experiments on the MURI 4 and 5 propellants showed a decrease in maximum response amplitude and a shift of the maximum response amplitude to a higher dimensional frequency with an increase in laser flux. This shift of the response amplitude with laser flux was not observed for this propellant though the data scatter coupled with the nearly constant response at low frequency could mask the shift of the threshold frequency to a higher dimensional frequency with the increase in laser flux.

In order to evaluate the decrease in response amplitude with laser flux, the condensed-phase heat release and gas-phase heat feedbacks were evaluated. The experimental temperature profiles did not show any difference in the temperature gradients in the gas-phase, and modeling efforts were not used due to the unknown compositions of these materials. Table 6-8 shows that the increase in laser flux increases the condensed-phase heat release from 170 to 177 cal/gm. The decrease in the propellant response with the increase in laser flux could be due to this small increase in the condensed-phase heat release, but it does not seem to be a large enough change to account for the difference.
For the case of a mean laser flux of 35 W/cm$^2$, the phase was zero and almost constant at driving frequencies ranging from 4 to 16 Hz and then decreased monotonically to a lag of 32 degrees at 96 Hz. At 60 W/cm$^2$, the phase was zero and almost constant for driving frequencies ranging from 4 to 20 Hz, and then decreased to a phase-lag of 19 degrees at 96 Hz. The phase signal is zero and nearly constant at the frequencies where the maximum amplitude response is measured. This shows consistency in the amplitude and phase measurements.
Figure 6-28 Pressure-driven Thrust Response for the AP/energetic binder propellant.
Figure 6-29 shows a comparison between the non-dimensional, pressure-driven, response amplitudes for the AP/energetic propellant and the baseline AP/HTPB (MURI 4) propellant. The AP/energetic propellant shows a near constant amplitude response at low frequency and a drop-off in response amplitude with an increase in frequency. The baseline AP/HTPB propellant shows a low response at low frequency, a maximum at “resonant” frequency and a drop-off with further increase in driving frequency. This behavior is typical of homogeneous propellants or propellants with small amounts of exothermic reactions in the condensed-phase. It should be noted that the baseline MURI 4 propellant (110 cal/gm) has a significant amount of exothermic heat release in the condensed-phase when compared to HMX (40 cal/gm). However the heat release in the AP/energetic binder (170 cal/gm) condensed-phase is significantly higher than the baseline MURI propellant (110 cal/gm). The baseline AP/HTPB propellant contains an inert binder and hence the clearly defined maximum response amplitude is probably due to the thermal relaxation time associated with the AP particles.

The energetic binder and the AP particles in the AP/energetic propellant could have different thermal relaxation times and hence maximum response amplitudes at different driving frequencies. The resulting heterogeneous AP/energetic propellant could thus have nearly constant response amplitude at low frequency. Tables 6-7 and 6-8 show that these AP/energetic binder propellants have significantly higher surface temperatures and heat release values in the condensed-phase. As discussed earlier, the higher heat release in the condensed-phase would results in a propellant that is less sensitive to changes at the condensed-phase, gas-phase interface and hence would have nearly constant response amplitudes. This is clearly visible in figure 6-28.
It should also be noted that the AP/energetic propellant response amplitudes are higher than that of the baseline AP/HTPB propellant at the same conditions. The AP/energetic propellant has maximum response amplitudes of 1.15 and 1, while the baseline has maximum amplitudes of 1.1 and 0.8 at incident heat fluxes of 35 and 60 W/cm² respectively. The energetic binders in the AP/energetic propellant are known to be intrinsically unstable at these test conditions and hence may result in the higher response amplitudes.

Figure 6-29 Comparison of Thrust Response Amplitudes for an AP/energetic propellant with its baseline during Pressure-Driven Combustion.

Figure 6-30 plots the response amplitudes for the AP/energetic propellants at 1, 2 and 3 atmospheres during self-deflagration. The figure shows that the response
amplitudes for the propellant decreases from 1.15 to 0.95 with an increase in pressure from 1 to 3 atmospheres. The previous chapter had shown that the thrust response profile would increase with pressure if the pressure exponent in the burning rate equation exceeded 0.5 (equation 5-21). For this propellant, the pressure exponent is 0.45 and hence is consistent with equation 5-21. The increase in pressure from 1 to 2 atmospheres increased the surface temperature from 920 to 1010 K and hence the condensed-phase heat release from 160 cal/gm to 205 cal/gm. The experimentally measured gas-phase temperature profiles did not show a change in the gas-phase temperature gradients with the pressure change. Hence the gas-phase heat feedback did not change significantly with pressure, while the exothermic heat release in the condensed-phase increased. Hence the lower response amplitudes at higher pressure are due to the increase in exothermic reactions in the condensed-phase.
6.3.3 AP and AP+AN-HTPE Propellants

Pressure-driven combustion experiments were conducted on the three HTPE based propellants at laser fluxes of 35 and 60 W/cm² at frequencies ranging from 4 to 96 Hz with the propellants placed in glass vials to obtain the desired one-dimensional response.

Figure 6-31 plots the non-dimensional thrust response amplitude for the three propellants at 35 and 60 W/cm². Figure 6-31(a) shows that with a laser flux of 35 W/cm², the amplitude response remains almost constant at low frequency and drops off
with an increase in driving frequency beyond the threshold frequency for both AP+AN propellants as well as the AP/HTPE propellant. For the AP+AN high rate propellant, the response amplitude decreased from 0.55 at 24 Hz to a value of 0.35 at 96 Hz at 35 W/cm$^2$, and decreased from 0.45 at 16 Hz to 0.25 at 96 Hz for the AP+AN low rate propellant. The AP/HTPE had the maximum response amplitude of the three propellants and its amplitude was near constant at 0.6 for frequencies ranging from 4 to 24 Hz, and then decreased to 0.35 at 96 Hz.

Figure 6-31 (b) plots the relative phase for the three propellants at a laser flux of 35 W/cm$^2$. For all three propellants, the relative phase is zero at low frequency and decreases to a lag of about 50 degrees with an increase in frequency. For all three propellants, the relative phase is not zero at the frequencies where the response amplitude is maximum. The relative phase for the AP/HTPE propellant lags by 6 degrees at 4 Hz and decreases to a lag of 15 degrees at 24 Hz. The response amplitude however stays constant at these frequencies. Hence these propellants do not display the classic QSHOD behavior that has propellants with zero relative phase at maximum response amplitude.
Figure 6-31 Pressure-driven Thrust response for the HTPE propellants at 35 W/cm²
Figure 6-32 plots the response amplitude for the three propellants at 60 W/cm$^2$. Similar to the test results at 35 W/cm$^2$, all three propellants have a near constant response amplitude at low frequency that drops off with an increase beyond a threshold driving frequency. The response amplitude for the AP+AN low rate propellant is nearly constant at 0.4 at driving frequencies of 4 to 16 Hz, and then decreases to 0.2 at 96 Hz. This response amplitude for the AP+AN low rate propellant appears to be slightly lower than its response at 35 W/cm$^2$. The AP+AN high rate propellant has a nearly constant amplitude response of 0.5 at driving frequencies ranging from 4 to 24 Hz and then decreases to 0.3 at 95 Hz. The response amplitude for this propellant is almost identical to its response at 35 W/cm$^2$. At 60 W/cm$^2$, the AP/HTPE propellant has the maximum response amplitude of the three propellants and has nearly constant amplitude of 0.57 at driving frequencies ranging from 4 Hz to 24 Hz, and then decreases to 0.35 at 96 Hz. The increase in laser flux results in a slightly lower amplitude response. Section 6.3.1 shows that the MURI 4 and 5 propellants exhibited a decrease in maximum response amplitude and a shift of the maximum response amplitude to a higher dimensional frequency with an increase in laser flux. This shift of the response amplitude with laser flux was not observed in these three propellants. Since the pressure-driven response experiments are carried out at discrete frequencies, it is possible that the shift of the response amplitudes with laser flux is undetected due to poor resolution in frequency. Also the decrease in response amplitude after crossing the threshold frequency is not very sharp. Hence the scatter in the data could mask the shift of the response amplitude to a higher dimensional frequency.
The pressure-driven response profiles at both laser fluxes for all three propellants are nearly constant at low frequency and then drop-off and frequencies beyond the threshold frequency. As discussed earlier, the three propellants have surface temperatures that are higher when compared to the AP/HTPB (MURI 4) propellant at similar test conditions. This suggests larger amounts of exothermic reactions in the condensed-phase. Tables 6-7 and 6-9 show that the condensed-phase heat release is much larger for these HTPE based propellants. Large amounts of exothermic reactions would result in a condensed-phase that is insensitive to variations in the dynamic phenomena at the surface/gas-phase interface and hence yield nearly constant response amplitudes at low frequency. The pressure-driven response profiles all exhibit nearly constant amplitudes at low frequency.
that drop off beyond the threshold frequency. This clearly suggests consistency between the steady-state temperature measurements and the unsteady pressure-driven experiments.

The steady-state temperature profiles for the HTPE based propellants did not detect any significant change in the surface temperature, heat release and gas-phase heat feedback with the change in laser flux. Since the propellant condensed-phase responds to changes in the gas-phase heat feedback and the condensed-phase heat release, the nearly constant heat feedback and heat release at both laser fluxes result in the similar response amplitudes.

Figure 6-33 compares the response amplitudes for the AP/HTPE propellant with an AP/HTPB and an AP/energetic binder propellant at a laser flux of 35 W/cm² during pressure-driven combustion. The AP/HTPB propellant shows a small response amplitude at low frequency, increases to its maximum and then decreases with a further increase in frequency, while the AP/HTPE and the AP/energetic propellants show a nearly constant response at low frequency that drops off after crossing a threshold frequency. The AP/HTPE and the AP/energetic propellants have maximum response amplitudes of 0.6 and 1.15 respectively, while the AP/HTPB propellant has maximum response amplitude of 1.1. The surface temperatures for the AP/HTPE, AP/energetic and AP/HTPB propellant are 1025, 950 and 750 K respectively. The higher surface temperature of the AP/energetic propellant as compared to the AP/HTPB propellant and the flat response amplitudes at low frequency are consistent with the temperature measurements for the AP and AP+AN/HTPE propellants and the hypothesis that the greater number of exothermic reactions in the condensed-phase result in constant response amplitudes at low frequency.
The AP/HTPE propellants have the lowest response amplitudes. This cannot be based simply on condensed-phase heat release or gas-phase heat feedback. The condensed-phase heat release is the lowest for the AP/HTPB propellant and the highest for the AP/HTPE propellant. If an increase in condensed-phase heat release resulted in a decrease in response amplitude, the AP/energetic binder propellant should have a response amplitude that is lower than the AP/HTPB propellant. Similarly the gas-phase heat feedback is the largest for the AP/HTPE propellant. If the gas-phase heat feedback is considered to be an amplifier, the HTPE based propellant should have the largest response.

![Figure 6-33 Response Amplitudes for AP/HTPE, AP/energetic and AP/HTPB during Pressure-Driven Combustion.](image)
Clearly there are chemical effects associated with the HTPE binder, the energetic binder and the HTPB binder that play a large role in determining the propellant response to an unsteady phenomenon. Hence it is imperative to develop a numerical model that captures the propellant combustion chemistry. This alone will allow predictive modeling of the measured response functions. Once the chemistry is validated, efforts should be made to use reduced kinetic models to obtain predictive response functions.

6.4 Comparison of Laser and Pressure-Driven Response Amplitudes

6.4.1 MURI 4 and 5

Figure 6-34 compares the laser and pressure-coupled response amplitudes for MURI#4 propellant during combustion at one atmosphere. The figure shows that both the laser and pressure coupled response functions have a peak at an omega of 8. The pressure coupled response functions have maximum amplitudes of 1.4 and 1.1 at heat fluxes of 35 and 60 W/cm², while the laser-coupled response functions have maximum amplitudes of 0.87 and 0.80 at the same laser fluxes. The response amplitudes decrease with an increase in laser flux for both the laser and pressure-driven combustion experiments.
Figure 6-34 Non-dimensional pressure and laser-driven response data for MURI#4 at one atmosphere.

Figure 6-35 compares the laser and pressure-coupled response amplitudes for MURI#5 propellant at one atmosphere. Both the laser and pressure coupled response functions have a peak at an omega of about 7. The pressure coupled response functions have maximum amplitudes of 1.35 and 1.0 at heat fluxes of 35 and 60 W/cm$^2$, while the laser-coupled response functions have maximum amplitudes of 0.85 and 0.80 at the same heat fluxes. The response amplitudes decrease with an increase in heat flux for both the laser and pressure-driven combustion experiments.
As discussed in section 6.2.1, the laser-driven experiments are condensed-phase response to the net unsteady flux incident on the propellant surface. The increase in laser flux decreases the mean component of the gas-phase heat feedback but increases the unsteady component. However the unsteady component of the gas-phase heat feedback is less than and out of phase with the unsteady laser flux. Hence the net unsteady flux decreases with the increase in laser flux resulting in the lower laser-driven response amplitudes. The pressure-driven experiments are the condensed-phase response to the gas-phase heat feedback. The mean and unsteady gas-phase heat feedback decrease with
the increase in laser flux. Table 6-11 shows that the unsteady heat feedback decreases by 25% with the increase in laser flux and results in a 22% change in the maximum response amplitude. The laser-driven response amplitude showed a significantly lower decrease in response amplitude (10%) due to the significantly smaller change in the unsteady component (6%) of the total flux incident on the surface.

6.4.2 AP/Energetic Propellant

Figure 6-36 compares the non-dimensional laser and pressure-driven thrust measurements. At 35 W/cm², the maximum pressure-driven response amplitude is 1.15 while the maximum laser-driven response amplitude is 0.75. The pressure-driven response amplitude is 50% higher than the laser-driven response amplitudes. The increase in the mean laser flux decreases the thrust response amplitude during pressure-driven combustion, but does not appear to change the thrust response amplitude during laser-driven combustion. This is once again an interesting result that needs to be studied with some caution.

The modeling results for the MURI propellants have shown that the unsteady component of the gas-phase heat feedback increases with the mean laser flux during laser-driven combustion. For the MURI propellants, the gas-phase heat feedbacks are 19 and 15 W/cm², while for the AP/energetic propellants; the heat feedback is 73 W/cm². If the unsteady component for this propellant also increases with the mean laser-flux, the propellant would have a larger unsteady flux incident on the propellant surface at the higher mean laser flux. However, the propellant also undergoes larger amounts of
exothermic reactions in the condensed-phase and hence the two mechanisms could negate each other resulting in the nearly constant response amplitude at both laser fluxes.

The modeling results for the MURI propellants have shown that the unsteady component of the gas-phase heat feedback decreases with an increase in laser flux during pressure-driven combustion. The decrease in the unsteady gas-phase heat feedback coupled with the larger amounts of exothermic reactions in the condensed-phase could result in the lower pressure-coupled response amplitudes at the higher mean laser flux. These hypotheses can only be qualitative because experimental data cannot provide the resolution required to detect subtle temperature gradients and modeling for these propellants is not possible without accurate information on its composition coupled with suitable gas-phase kinetic mechanisms.
6.4.3 AP and AP+AN/HTPE Propellants

Figures 6-37 (a) and (b) plot the response amplitudes during laser and pressure-driven combustion for the three propellants at 35 and 60 W/cm\(^2\). The open symbols are the data associated with pressure-driven combustion, while the closed symbols represent laser-driven combustion. Figure 6-37 (a) shows that the pressure-driven response amplitudes are higher than the laser-driven response amplitudes for all propellants. For the AP/HTPE propellant, the pressure-driven response amplitudes are nearly constant at 0.6 from an \(\Omega\) of 1.8 to 10, and then decreases to 0.35 at an \(\Omega\) of 43, while the laser-driven response increases slightly from 0.37 at an \(\Omega\) of 1.8, to 0.41 at an \(\Omega\) of 8, and then
decreases to 0.25 at an $\Omega$ of 60. The laser-driven response amplitude shows a small increase with frequency at low frequency, while the pressure-driven response data is nearly constant at low frequency. The pressure-driven response amplitude for the AP+AN high rate propellant is constant at 0.5 for $\Omega$ values ranging from 2 to 10, and then decreases to 0.35 at an $\Omega$ of 40, while the laser-driven response amplitude is constant at 0.35 for $\Omega$ values from 2 to 10 and then decreases to 0.20 at an $\Omega$ of 55. Both the laser and pressure-driven responses have similar profiles with the pressure-driven response being much larger in magnitude. The pressure-driven response for the AP+AN low-rate propellant is also constant at 0.45 from $\Omega$ values of 4 to 13 and then decreases to 0.25 at an $\Omega$ value of 80. The laser-driven responses also stay constant at 0.35 for $\Omega$ values ranging from 3.5 to 19, and then decrease to 0.2 at an $\Omega$ value of 210. The pressure-driven response amplitudes are higher than the laser-driven case. For the AP+AN low rate propellants, the non-dimensional threshold frequency for the pressure-driven tests is 13 as compared to 19 for the laser-driven experiments.

Figure 6-37 (b) plots the response amplitudes for the three propellants at a mean laser flux of 60 W/cm$^2$. The most important finding for these propellants is the effect of the mean laser flux on the laser and pressure-driven response amplitudes. Figures 6-31(a) and 6-32 showed that the increase in laser flux resulted in either a small decrease or no change in the pressure-driven response amplitude. Figure 6-37 (a) and (b) show that the increase in the laser flux results in a significant increase in the laser-driven response amplitude. For the AP/HTPE propellants, the pressure-driven response amplitudes are near-constant at 0.57 for $\Omega$ values ranging from 1.5 to 8, and then decrease to 0.35 at a $\Omega$
value of 31, while the laser-driven response amplitudes increase from 0.57 at an $W$ of 1.25, to 0.63 at an $\Omega$ of 7.5, and then decrease to 0.45 at an $\Omega$ of 78. The pressure-driven response amplitudes are lower than the laser-driven case. Also the pressure-driven response amplitude is nearly constant at low frequency, while the laser-driven response amplitudes increase at low frequency to a maximum and then decrease with a further increase in frequency. The AP+AN/HTPE high rate propellant has a pressure-driven response amplitude of 0.46 for $\Omega$ values ranging from 1.5 to 10, and then decreases to 0.33 at an $\Omega$ value of 35. The laser-driven response amplitude is also constant at 0.53 for $\Omega$ values of 1.5 to 10, and then decreases to 0.3 at an $\Omega$ of 82. The pressure-driven response amplitudes are lower than the laser-driven response amplitudes but exhibit similar characteristics. The pressure-driven response for the AP+AN low rate propellant decreases from 0.4 at an $\Omega$ of 13, to 0.225 at an $\Omega$ of 52, while the laser-driven response decreases from 0.47 at an $\Omega$ of 12, to 0.25 at an $\Omega$ of 150. Once again, the pressure-driven response amplitudes are lower than the laser-driven response.

In order to understand this behavior of the response amplitude with the increase in laser flux, the driving mechanisms that lead to unsteady combustion are evaluated. A variation in the ambient pressure/heat flux results in a variation in the gas-phase heat feedback to the propellant surface and hence results in a condensed-phase response to this time variant heat feedback. For all three propellants, video images show the propellant flame to be very close to the propellant surface for both laser fluxes, and steady-state experiments have shown that the increase in laser flux results in an increase in the burning rate but does not increase the flame standoff distance. The temperature
measurements also show that the increase in laser flux does not appear to change the gas-phase heat feedback. For all three propellants, the pressure-driven response amplitude does not change significantly with an increase in laser flux and suggests that the unsteady gas-phase heat feedback and condensed-phase heat release are almost constant with the increase in the mean laser flux.

During laser-driven tests, the laser is modulated at a heat flux of ±15 W/cm². The thermal conductivity of the gas-phase is assumed to be $2.4 \times 10^{-4} \text{cal/cm-s-°C}$ [101] and the gas-phase temperature gradient is approximately $10^5 \text{°C/cm}$ resulting in a steady-state gas-phase heat feedback of 100 W/cm². As discussed earlier, the experimental data suggests that the increase in the mean laser flux does not appear to affect the steady-state gas-phase heat feedback. Modeling results on the MURI 4 and 5 propellants have shown that the unsteady gas-phase heat feedback increases with the increase in laser flux during laser-driven combustion. Since the heat feedback for these propellants is five times larger than the MURI propellants, an increase in the gas-phase heat feedback could result in the larger propellant response amplitudes especially considering the nearly constant exothermicity in the condensed-phase at both laser fluxes.

It is also possible that the increase in response amplitude with the increase in laser flux could be due to some non-linear effects associated with the large unsteady heat flux values used in the experiments. At a mean laser-flux of 35 W/cm², the laser-driven experiments provide an unsteady peak-to-peak heat flux that is 86% of the mean, while at 60 W/cm², the unsteady heat flux is 50% of the mean.
Figure 6-37 Thrust Response Amplitudes versus non-dimensional frequency during Laser and Pressure-driven combustion at 35 and 60 W/cm² for the HTPE propellants.
6.5 Comparison of experimental response with a theoretical function

The transfer function developed by Brewster et al. will be compared to the response functions for the MURI 4 and 5 propellants. Since the transfer function is based on the ZN model and does not account for the large amounts of exothermic reactions in the condensed-phase, this function will not be applied to the AP/energetic propellants.

Figures 6-38 and 6-39 compare the response functions for the MURI 4 and 5 propellants at 35 and 60 W/cm$^2$ against the transfer function developed by Son et al and developed in equation 5-22 and 5-23.

![Graph](image)

**Figure 6-38** Transfer function versus ratio of Response functions for MURI 4 and 5 propellants at 35 W/cm$^2$. 
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Table 6-12 List of parameters used in the transfer function

Figure 6-39 Transfer function versus ratio of Response functions for MURI 4 and 5 propellants at 60 W/cm².
Figure 6-38 shows that the experimental ratios of pressure and laser-driven response are scattered and have a value of ~ 1.7 for both propellants. The transfer function predicts a ratio of 1 at an $\Omega$ of 2 that decreases to 0.85 at an $\Omega$ of 30. Clearly the experimental and theoretical ratios are in poor agreement despite the scatter in the data.

Figure 6-39 plots the experimental ratios for the MURI propellants at 60 W/cm$^2$ against the transfer function. The figure shows that the experimental ratios increase from 1.5 for the MURI propellants at an $\Omega$ value of 1.8, to 1.9 at an $\Omega$ value of 22 for the MURI 4 propellant. The MURI 5 propellant has a nearly constant response ratio of 1.5 for $\Omega$ values ranging from 1.8 to 25. The transfer function however predicts ratio of 0.95 at an $\Omega$ value of 1.8 that decreases to 0.9 at an $\Omega$ value of 22.

The transfer function under-predicts the ratios of the pressure and laser-driven response functions at both heat fluxes. The transfer function is clearly an excellent idea if the driving mechanisms are consistent in the two experimental techniques. The previous sections have demonstrated that the laser and pressure-driven experiments are not analogous to each other. Hence this transfer function should not be used as a tool to obtain pressure-driven response data based on laser-driven experiments.

Clearly the assumptions in the ZN method make the use of such transfer functions difficult for complex propellants with considerable amounts of condensed-phase heat release. These transfer functions should only be used as a qualitative tool. Hence comparisons with the experimental data for the AP/energetic binder and the HTPE based propellants are not included in this study.
6.6 Comparison of Response with an Analytical function

Figure 6-40 plots the variation in surface temperature for MURI 4 at 1 atmosphere during self-deflagration in air. The surface temperature measurements are difficult to interpret partially due to the heterogeneous nature of these propellants. However it is still useful to attempt a comparison between the analytical functions based on the experimental steady-state data and the experimentally measured pressure-driven response data.

![Figure 6-40 Surface temperature during pressure-driven combustion at 101 KPa](image)
The maximum and minimum surface temperatures were 720 and 765 K. This resulted in burning rate fluctuations of 0.08 mm/s and hence a response amplitude of 0.75 at 4 Hz. The measured pressure-driven response amplitude for this propellant is 0.96. With the uncertainties in the surface temperature, the gas-phase heat feedback and the unsteady pressure-driven response measurements, this comparison appears to be quite reasonable. Clearly the inclusion of the condensed-phase heat release and the gas-phase heat feedback in the burning rate equation result in a more realistic and physical response amplitude. However this method cannot be readily used for most AP composite propellants due to the difficulties in obtaining transient temperature measurements. Hence a model with detailed mechanisms that account for the condensed-phase heat release and the gas-phase heat feedback and heat release are vital steps that need to be taken to obtain a predictive model.
Chapter 7

SUMMARY AND RECOMMENDATIONS

7.1 Summary

A pressure driven combustion facility was developed and used to measure pressure-coupled amplitude and phase response during combustion of propellant samples at low pressure. Performing laser-driven experiments in this rig and comparing them to the laser-driven experiments performed in the laser driven combustion test chamber validated the data acquisition systems. The laser and pressure-driven chambers were used to obtain thrust response amplitude and phase information during the combustion of HMX and heterogeneous AP composite propellants at one, two and three atmospheres. The CO₂ laser was used to ignite and sustain combustion as well as provide the oscillatory heat flux during laser-driven combustion. This summary will be divided into two sub-sections covering the results for HMX and the AP composite propellants.

The overall principal objectives and issues that were addressed in this study were:

1) Build an experimental setup to measure pressure-driven response for solid propellants.

2) Obtain experimental response data during laser and pressure-driven experiments at the highest possible test pressures with and without laser flux.
3) Compare the experimentally obtained FM parameters with steady-state data to help validate the response measurements. The goal was to perform an “in the ball park” analysis.

4) Compare the data with numerical and analytical modeling efforts to help with validation.

5) Identify the effects of energetic additives and binders on the response behavior of the propellants.

6) Compare the experimental laser and pressure-coupled response functions with the theoretical transfer function developed by Son et al.

7.1.1 HMX

Steady-state surface temperature and energy balance analyses were used to evaluate the effects of condensed-phase heat release and the gas-phase heat feedback on the propellant response during laser and pressure-driven experiments. The one-dimensional energy balance used the assumption that the heat release occurred in a small region of the propellant condensed-phase called the surface reaction zone. The surface and near-surface temperature profiles showed that at a given pressure, the increase in laser flux resulted in a small increase in the surface temperature, a greater flame stand-off distance and hence a lower gas-phase heat feedback. At a given laser flux, the increase in pressure resulted in higher gas-phase heat feedback and greater exothermicity in the condensed-phase. One-dimensional modeling through Chemkin showed reasonable agreement with
the measured steady-state species data and hence was used to interpret the effects of laser flux on the steady and unsteady components of the gas-phase heat feedback.

The laser-driven combustion experiments on HMX showed that at 1 atmosphere, an increase in laser flux from 35 to 60 W/cm² resulted in nearly constant thrust response amplitudes, but a further increase in laser flux lowered the response amplitudes. The increase in the laser flux results in larger steady components of the total flux incident on the propellant surface, while the unsteady component of the laser flux remains almost constant. There is a small increase in the surface temperature and hence greater probability for the endothermic reactions in the propellant condensed-phase at the higher laser flux. Hence the lower response amplitudes could be due to this decrease in exothermicity in the propellant condensed-phase. Laser-driven experiments at higher pressure showed that the response amplitudes decreased with the increase in pressure. This decrease in response was due to the increase in the unsteady component of the gas-phase heat feedback. Since the gas-phase heat feedback is out of phase with the laser flux, the increase in the unsteady gas-phase heat feedback resulted in lower unsteady components of the net flux incident on the propellant surface. Since the unsteady component of the laser flux is constant and larger than the unsteady component of the gas-phase heat feedback, changes in the unsteady heat feedback result in only small changes in the net unsteady flux and hence result in small decreases in the response amplitudes with the increase in ambient pressure. For all cases, the response amplitudes shifted to higher dimensional frequencies with an increase in laser flux or pressure. This suggested that the frequency of maximum condensed-phase response is a function of the burning rate. Plots of the response amplitudes versus non-dimensional frequency showed
that the maximum response amplitudes were observed at nearly constant values of the non-dimensional frequency despite changes in pressure and laser flux. The non-dimensional frequency is a product of the condensed-phase thermal relaxation time and the driving frequency and the nearly constant non-dimensional frequency at different laser fluxes and pressures suggested that the propellant maximum response amplitudes were a function of the condensed-phase thermal relaxation.

The pressure-driven experiments showed that the response amplitudes decreased with an increase in laser flux. The pressure-driven experiments are primarily a condensed-phase response to the unsteady gas-phase heat feedback. At a given pressure, an increase in laser flux results in lower steady and unsteady components of the gas-phase heat feedback. The increase in laser flux also increases the surface temperature and decreases the exothermic heat release in the condensed-phase. Hence the lower propellant responses are due to the decrease in gas-phase heat feedback and heat release in the condensed-phase. The propellant response amplitudes also shifted to a higher dimensional frequency with the increase in laser flux due to the thermal relaxation effect. At any given laser flux, an increase in the ambient pressure resulted in higher response amplitudes due to the higher unsteady components of the gas-phase heat feedback. In addition to the increase in heat feedback, the increase in pressure could also result in a greater amount of endothermic decomposition in the two global decomposition reactions and greater amount of exothermicity in the secondary reactions. As discussed earlier higher reactions rates for the endothermic global decomposition and exothermic secondary reactions could result in a larger build-up and consumption of the intermediate decomposition products in the condensed-phase. Hence larger reaction rates for these
reactions could result in larger variations in temperature and burning rate and hence larger response amplitudes. In addition to the higher response amplitudes at higher pressures, the pressure-driven response profiles were also “flatter” at low frequency due to the increase in condensed-phase heat release.

Comparison with the analytical model of Culick shows that the experimental response values are significantly higher than the predictions of the analytical model. This is partially due to the simplifying assumptions (Arrhenius burning rate, simplified gas-phase parameter) used to obtain the expression. The model predicts that for a fixed gas-phase parameter, the increase in condensed-phase heat release results in lower response. However suitable changes to the gas-phase parameter show that an increase in heat release could result in larger condensed-phase response values and are consistent with experimental measurements for the pressure-driven response. Comparisons of the experimental response amplitudes with the analytical expression developed by Iribicu and Williams showed reasonable agreement. This is partially due to the dependence on the steady-state experimental and modeling data that are used in the expression for instantaneous burning rate. Since the effect of the gas-phase heat feedbacks and condensed-phase heat release are captured through these experimental measurements, the analytical model provided a reasonable agreement with experimental data. It is extremely difficult to obtain transient temperature profiles and heat feedbacks at motor pressures. Hence detailed modeling efforts that capture the effects of gas-phase heat feedback and condensed-phase heat release are essential towards obtaining a fundamental understanding of the coupling between ambient pressure fluctuations and the propellant response.
Comparisons between laser and pressure-driven data show that the experiments measure condensed-phase responses of the propellant to different driving phenomena. The pressure-driven experiments are primarily a condensed-phase response to the unsteady gas-phase heat feedback, while the laser-driven experiments are condensed-phase responses to the total unsteady flux. Hence the pressure-driven response amplitudes increased with pressure, while the laser-driven response amplitudes decreased with pressure. Due to the different driving mechanisms for laser and pressure-driven combustion, the two experiments are not analogous to each other. Comparisons of the experimental data with the theoretical transfer function of Son and Brewster showed that the transfer function under-predicted the experimental ratios and should not be used as a means to obtain pressure-driven response based on laser-driven response measurements.

Table 7-1 lists the effect of changes to various parameters on the laser and pressure-driven response amplitudes for HMX. The table summarizes the observations that the pressure increase results in higher pressure-driven response amplitudes but lower laser-driven response amplitudes. It also lists the effect of pressure and laser flux on the heat feedback and condensed-phase heat release.
<table>
<thead>
<tr>
<th></th>
<th>Increase in Pressure</th>
<th>Increase in Laser flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p$</td>
<td>Amplitude increases significantly</td>
<td>Amplitude decreases significantly</td>
</tr>
<tr>
<td>$R_q$</td>
<td>Small decrease in amplitude</td>
<td>Small decrease in amplitude</td>
</tr>
<tr>
<td>Steady-State</td>
<td>Increases from 3 to 8 W/cm$^2$ with pressure increase of 1 to 3 atm.</td>
<td>Decreases from 8 to 6 W/cm$^2$ with laser flux from 35 to 60 W/cm$^2$</td>
</tr>
<tr>
<td>Heat release</td>
<td>Increases from 38 to 46 cal/gm</td>
<td>Decreases from 46 to 39 cal/gm</td>
</tr>
</tbody>
</table>

Table 7-1 Effect of ambient conditions on response amplitudes, heat feedback and condensed-phase heat release.

7.1.1.1 Contributions of this Study

This study clearly showed that the laser and pressure-driven experiments are driven by the net unsteady flux and the unsteady gas-phase heat feedbacks that are incident on the propellant surface. The different driving mechanisms showed that the two experiments are not analogous and resulted in different propellant behavior to changes in the ambient conditions during laser and pressure-driven combustion. This study also quantified the effects of the mean and unsteady components of the heat feedback and the condensed-phase heat release on the laser and pressure-driven response amplitude. An investigation of the analytical modeling showed the inability to accurately predict the effects of pressure and exothermic heat release on the propellant response profiles. The importance of the gas-phase heat feedback and the condensed-phase heat release in the development of a response function were clearly visible through the analytical model of Iribicu and Williams that showed good agreement with the experimental data. The study
also documented the possibility of coupling between gas-phase heat feedback and
condensed-phase self-oscillatory behavior for HMX. Such coupling can only be
evaluated through detailed models that capture the condensed-phase and gas-phase
chemical kinetics. The inability of the ZN method to account for condensed-phase
decomposition resulted in a transfer function that was limited in its application. Hence
the study showed that rigorous numerical models are essential towards obtaining
predictive models for pressure-driven response functions.

7.1.2 Heterogeneous Propellants

Steady-state temperature measurements and one-dimensional energy balance
analyses were used to understand the effect of condensed-phase heat release on the
response amplitudes. The temperature measurements for the baseline MURI 4 and 5 and
the AP/energetic binder propellants showed a slight increase in surface temperature with
laser flux, while the AP and AP+AN/HTPE based propellants showed nearly constant
surface temperatures at both laser fluxes. The steady-state energy balance showed that
the condensed-phase exothermic heat release for the three sets of propellants increased
with an increase in laser flux or pressure.

7.1.2.1 Laser-Driven Combustion

The MURI 4 and 5 propellants showed that the increase in mean laser flux during
laser-driven combustion resulted in lower response amplitudes. The modeling results
suggest that the increase in the mean laser flux results in a lower steady-state component
of the gas-phase heat feedback, but a higher unsteady component of the gas-phase heat
feedback. Since the unsteady laser flux and gas-phase heat feedback are out of phase, an increase in the unsteady gas-phase heat feedback results in a lower net unsteady flux on the propellant surface. The increase in mean laser flux resulted in lower net unsteady laser fluxes incident on the propellant surface and increased the condensed-phase exothermicity and hence resulted in lower response amplitudes.

The measurements on the AP/energetic binder propellants showed that the response profiles were nearly constant at low frequency and decreased in amplitude beyond the threshold frequency. The steady-state measurements and analyses showed that the surface temperatures and heat release were significantly greater than the base line MURI 4 and 5 propellants. This condensed-phase exothermicity resulted in a condensed-phase that is less sensitive to the dynamic changes at the gas-phase/condensed-phase interface and hence produces the nearly constant response amplitudes at low frequency. The response amplitudes also did not decrease with an increase in laser flux. The experimental gas-phase profiles show that the steady-state component of the heat feedback does not change with the increase in laser flux. Hence it is assumed that the unsteady component of the heat feedback also does not change with the mean laser flux. The condensed-phase responds to the unsteady component of the total flux incident on the propellant. This unsteady component is assumed to be constant at both laser fluxes and result in the similar response amplitudes. The nearly constant response amplitudes at both laser fluxes could also be due to the increase in unsteady heat feedback being off-set by the increase in exothermic reactions in the condensed-phase.

The AP and AP+AN/HTPE propellants have large uncertainties in the surface temperature measurements that do not allow for measurement of surface temperatures as
a function of laser flux. The laser-driven response amplitudes for these propellants increase with an increase in laser flux. The gas-phase heat feedbacks for these propellants are higher than the AP/energetic and the MURI 4 and 5 propellants and an increase in the laser flux might increase the unsteady gas-phase heat feedback resulting in the larger response amplitudes. The larger response amplitudes at higher frequency could also be due to some non-linearities associated with the high oscillatory components of the laser flux.

Table 7-2 summarizes the effects of changes in laser flux on the laser-driven response amplitudes, the condensed-phase heat release and the gas-phase heat feedback for the AP composite propellants.

<table>
<thead>
<tr>
<th>Test Parameter</th>
<th>MURI 4,5</th>
<th>AP/energetic</th>
<th>AP/HTPE</th>
<th>AP+AN/HTPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response Amplitude</td>
<td>Decreases with increase in laser flux</td>
<td>Unchanged with increase in laser flux</td>
<td>Increases with increase in laser flux</td>
<td>Increases with increase in laser flux</td>
</tr>
<tr>
<td>Condensed-phase heat release (cal/gm)</td>
<td>Increases with laser flux (120-140)</td>
<td>Small increase with laser flux (160-180)</td>
<td>Almost unchanged with laser flux (190)</td>
<td>Almost unchanged with laser flux (185)</td>
</tr>
<tr>
<td>Steady-State Heat Feedback (W/cm²)</td>
<td>Decreases with increase in laser flux (~20)</td>
<td>Unchanged with laser flux (~70)</td>
<td>Unchanged with laser flux (~100)</td>
<td>Unchanged with laser flux (~100)</td>
</tr>
</tbody>
</table>

Table 7-2 Effect of laser flux on laser-driven Response Amplitudes, condensed-phase heat release and heat feedback.
7.1.2.2 Pressure-Driven Combustion

The pressure-driven response amplitudes for the MURI 4 and 5 propellants decreased with the increase in laser flux because of the decrease in the unsteady gas-phase heat feedback coupled with the increase in the condensed-phase heat release. The pressure-driven response amplitudes for the MURI propellants were higher than the laser-driven response. The increase in pressure from 1 to 3 atmospheres resulted in lower response amplitudes and response profiles that were nearly constant at low frequency. The steady-state data shows that the exothermicity in the condensed-phase increased with pressure. Hence the increase in condensed-phase heat release resulted in a condensed-phase that was less sensitive to dynamic changes at the condensed-phase/gas-phase interface and resulted in the lower response amplitudes at the higher pressures and the “flat” response amplitude profiles. This hypothesis is consistent with the steady-state temperature measurements and energy balance analysis. Flowmeter data from Micci et al. detected maximum response amplitudes at an $\Omega$ value of 15-20 and is in good agreement with the recoil measurements. It should be noted that the response functions differ in magnitude. However it is possible that the difference in magnitude of the response function was due to the peculiar burning rate behavior of the MURI 4 and 5 propellants. The MURI 5 flow meter response at 20 atmospheres at $\Omega$ values of 5-8 was quite close to the MURI 5 response obtained from the recoil tests at 3 atmospheres.

Comparisons with the modeling effort of Culick show that the experimental response functions for the MURI 4 and 5 propellants were much larger than the predicted values.
However, the model did capture the trend of decreasing response functions with an increase in condensed-phase heat release.

The AP/energetic propellants also decreased in response amplitude at the higher laser flux due to the increase in the condensed-phase heat release. Comparisons with the MURI 4 and 5 propellants showed that the response amplitudes for the AP/energetic propellant are nearly constant at low frequencies due to the higher surface temperatures and greater exothermicity in the propellant condensed-phase. An increase in pressure from 1 to 3 atmospheres also resulted in lower response amplitudes due to the increase in the condensed-phase heat release.

The AP and AP+AN/HTPE propellants had nearly constant response amplitudes at both laser fluxes. The surface temperature, the gas-phase heat feedback and the condensed-phase heat release appeared to be nearly constant at both laser fluxes and hence resulted in the nearly constant response amplitudes.

The laser-driven experiments measured the response of the propellant condensed-phase to the sum of the unsteady gas-phase heat feedback, and the unsteady laser flux, while the pressure-driven experiments measure the condensed-phase response to the unsteady gas-phase heat feedback. Comparisons between the laser and pressure-driven response amplitudes showed that the different driving mechanisms resulted in a different response to the changes in laser flux for the three sets of propellants. The MURI 4 and 5 propellants show a decrease in response amplitude during both laser and pressure-driven combustion with an increase in laser flux. The AP/energetic propellant had nearly constant response amplitudes during laser-driven combustion while the response amplitudes decreased with an increase in laser flux during pressure-driven combustion.
The HTPE based propellants had an increase in response amplitude with laser flux during laser-driven combustion, but had nearly constant response amplitudes during pressure-driven combustion. Hence the laser and pressure-driven experiments cannot be considered as analogous.

<table>
<thead>
<tr>
<th></th>
<th>MURI 4,5</th>
<th>AP/energetic</th>
<th>AP/HTPE</th>
<th>AP+AN/HTPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase in laser flux</td>
<td>Decreases</td>
<td>Decreases</td>
<td>Small decrease</td>
<td>Small decrease</td>
</tr>
<tr>
<td>Increase in Pressure</td>
<td>Decreases</td>
<td>Decreases</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>$R_p$ Vs $R_q$ as a function of laser flux (35 and 60 W/cm$^2$)</td>
<td>$R_p$ greater at both fluxes</td>
<td>$R_p$ greater at both fluxes</td>
<td>$R_p$ greater at 35, $R_q$ greater at 60</td>
<td>$R_p$ greater at 35, $R_q$ greater at 60</td>
</tr>
</tbody>
</table>

Table 7-3 Effect of laser flux and pressure on Pressure-Driven Response Amplitudes.

Table 7-3 summarizes the effect of laser flux and pressure on laser and pressure-driven response amplitudes. The table also compares the amplitudes of laser and pressure-driven response as a function of mean laser flux. The table clearly shows that the laser-driven and pressure-driven response amplitudes show different effects to changes in laser flux for the HTPE propellants.

### 7.1.2.3 Comparisons with the theoretical transfer function

Comparison of the experimental laser and pressure-driven response functions with the theoretical transfer function of Son et al. showed that the transfer function under predicts the experimental ratios by 50-70%. The transfer function appears to decrease with the increase in frequency, while the experimental ratio increases with frequency. Hence the limitations in the ZN method result in a transfer function that is limited in use
and should not be used as a tool to obtain pressure-driven response functions based on laser-driven experiments.

The analytical model of Iribicu and Williams and Roh et al. resulted in response amplitudes that were close to the experimental values for the MURI 4 propellants. However difficulties in the experimental measurements of surface temperatures and heat feedback result in limited use of these analytical models. Hence it is highly desirable to develop a comprehensive model that incorporates the fundamental mechanisms that govern propellant response and delivers predictive response functions without using experimental data. However experiments are critical in validating such models and should continue to be a focal point of research efforts.

7.1.2.4 Contributions of this Study

The laser and pressure-driven response experiments showed that the different driving mechanisms (unsteady net flux and unsteady gas-phase heat feedback) resulted in different effects of changes in the ambient conditions on the response amplitudes. Hence these experiments are not analogous. Due to small variations in the gas-phase heat feedback with pressure, the analytical model was able to qualitatively predict the trend of pressure-driven response with an increase in laser flux and pressure. The experimental data for the AP/energetic binder propellant showed a response amplitude that was significantly higher than the AP/HTPE propellants. The condensed-phase heat release and gas-phase heat feedback for the AP/HTPE propellant was only 10% higher than the AP/energetic binder propellant. Hence the HTPE binder might result in decomposition pathways in the condensed-phase that are unaffected by changes in the ambient
conditions. Hence this study clearly identified the need for rigorous chemical studies and numerical models that incorporate the appropriate chemical kinetics for the propellants. Hence it is important to avoid lumping all heterogeneous parameters into a simple two or three parameter response function that only account for effects of surface temperature, burning rate exponent and temperature sensitivity. This study also showed the limitations of the ZN framework and hence the transfer function in prediction of experimental ratios of laser and pressure-driven response functions. A transfer function would be useful if it accounted for the effects of condensed-phase heat release and binder ingredients, properties and kinetic mechanisms.

7.2 Recommendations for Future Work

Some of the future work to be performed in this study are listed below:

1. Perform pressure-coupled response measurements at realistic pressures. An increase in the ambient pressure will suppress some reactions and enhance others. Burn rate response coupled with surface temperature measurements at higher pressure will help develop a link between the reaction mechanisms and the combustion response of the propellant. It is important to ensure that the mechanisms studied hold true at realistic rocket operating pressures. An improved understanding of the propellant behavior during dynamic combustion can thus be achieved through testing at multiple pressure conditions.

2. Modify the system to perform experiments at higher driving frequencies. The current system is limited to an operating frequency of 100 Hz and is lower than the
fundamental longitudinal mode oscillations that are detected in the rocket motors. It may be necessary to use different acoustic drivers to obtain the higher frequencies. Acoustic drivers that are used in the gas-turbine industry are expensive and provide peak-to-peak amplitudes of 2-3 psi. These pressure amplitudes are relatively low and may not be useful for rocket motor experiments. Some efforts should focus on development of drivers and transducers that can obtain and detect 10% peak-to-peak variations in pressure at elevated pressures.

3. Stop the laser-driven experiments and improve the pressure-driven experiments. This study has shown that the laser and pressure-driven experiments have different driving mechanisms. Hence it is of little use to perform “artificial” laser-driven response experiments. The emphasis on the pressure-driven experiments at realistic pressures will help evaluate the driving and damping mechanisms that result in the propellant response.

4. The poor agreement with the data of Beckstead and Erikson could be due to poorly defined condensed-phase reactions. The possibility of condensed-phase self-oscillatory behavior in addition to gas-phase coupling could explain the differences between the measured and predicted response amplitudes. Does changing the temperature sensitivity parameter alone make up for the difference (as suggested by Erikson)? Some effort towards developing better condensed-phase kinetics will help improve the predictive abilities of the model.

5. Identify other research groups working in modeling of combustion instability. Provide the AP/HTPB gas-phase mechanism used in this study and evaluate the feasibility of detailed modeling of these heterogeneous propellants.
BIBLIOGRAPHY


83. Series 57/60 Lasers Operation and Service Manual, SYNRAD.


103. Melius, C.F., in Chemistry and Physics of Energetic Materials (edited by S.N. Bulusu) 1990 p. 21


APPENDIX A

Derivation of $R_p$ using the FM approach

Some of the assumptions used in the FM approach are:

1. The gas-phase during unsteady combustion reacts instantaneously to any changes and can be assumed to be quasi-steady
2. The propellant is homogeneous
3. The solution is one-dimensional
4. The propellant response is linear (small perturbations and product of perturbations are negligible)
5. Constant material properties in the condensed phase.
6. No chemical reactions in the condensed phase. (some models relax this assumption)
7. The propellant releases energy in a single plane in the gas-phase. (Von Karman flame sheet) {Some models use an energy release in a finite region in the gas-phase.}

This approach breaks the combustion process down into three regions; the gas-phase, the solid phase and the interface. The approach uses an inertial system of reference with the solid moving towards the burning surface at rate $r$ (the steady state burning rate)

A.1 Solid Phase Region

The solid phase equation reduces to the energy equation and can be written as

$$\lambda_p \left( \frac{\partial^2 T}{\partial x^2} \right) - \bar{m} c \left( \frac{\partial T}{\partial x} \right) - \rho_p c \left( \frac{\partial T}{\partial t} \right) = -\dot{Q}_d$$  \hspace{1cm} [A-1]
where $\dot{Q}_d$ is the heat generation per unit volume.

In this approach we will assume $\dot{Q}_d$ is zero.

The initial and boundary conditions are described by equation \[A-2\]

\[
T(x,0) = T_0 \\
T(-\infty,t) = T_0 \\
T(0,t) = T_s(t)
\]

The above equation is non-dimensionalized using the relationships shown in equation \[A-3\]

\[
\theta = \frac{T - T_0}{T_s - T_0} \quad \tau = \frac{\ddot{u}_p t}{\alpha} \quad \xi = \frac{\ddot{u}_p x}{\alpha} \quad V = \frac{u_p}{\ddot{u}_p} \quad \alpha = \frac{\lambda_p}{\rho_p C_p}
\]

The equation reduces to

\[
\left(\frac{\partial^2 \theta}{\partial \xi^2}\right) = \left(\frac{\partial \theta}{\partial \tau}\right) + V \left(\frac{\partial \theta}{\partial \xi}\right)
\] \[A-4\]

The steady state solution is given by equation \[A-5\]

\[
\bar{T}(x) - T_0 = (T_s - T_0) \cdot \exp\left(\frac{\ddot{u}_p x}{\alpha}\right)
\]

The solution can also be written as

\[
\bar{\theta} = e^{\xi}
\] \[A-6\]

The variables are considered to be complex quantities with a mean value and an oscillatory component. The pressure is assumed to oscillate harmonically and the resulting equations for temperature and burning rate are given by equation \[A-7\].
\( \theta = \bar{\theta} + \theta' e^{i \alpha \tau} = 1 + \theta' e^{i \alpha \tau}, \quad V = \bar{V} + V' e^{i \alpha \tau} = 1 + V' e^{i \alpha \tau}, \quad \Omega = \frac{\alpha \omega}{\bar{u}_c} \) 

Equation A-7 is substituted back into A-4 and the small perturbations are neglected to get equation A-8.

\[
\left( \frac{\partial^2 \theta'}{\partial \xi^2} \right) - \left( \frac{\partial \theta'}{\partial \xi} \right) - i \Omega \theta' = V' e^{i \xi} \tag{A-8}
\]

where \( \theta'(-\infty) = 0 \) \( \theta'(0) = \theta_s' \) \tag{A-9}

Since the oscillatory motions are harmonic, the spatial dependence is determined from A-4 and is of the order of \( \exp(\lambda \xi_p) \). \( \lambda \) satisfies equation A-10.

\( \lambda(\lambda - 1) = i \Omega \) \tag{A-10}

\( \theta' = A e^{\lambda \xi} + B e^{\lambda \xi} + \frac{i V'}{\Omega} e^{\xi} \) \tag{A-11}

The boundary conditions show that \( B = 0 \) and hence the equation can be written as A-12.

\( \theta' = A e^{\lambda \xi} + \frac{i V'}{\Omega} e^{\xi} \) \tag{A-12}

\( \lambda \) can be broken down into real and imaginary parts and can be written as A-13

\( \lambda = \frac{1}{2} + \frac{\Omega}{2R} + i R \) \tag{A-13}

\[ R = \frac{1}{2\sqrt{2}} \sqrt{16\Omega^2 + 1} - 1 \]

To evaluate \( A \) in equation A-12, we use the second boundary condition and find that
\[ \theta' = \left( \theta_s - \frac{iV'}{\Omega} \right) e^{\xi} + \frac{iV'}{\Omega} e^{\xi} \]  

The temperature gradient below the surface is given by A-15

\[ \frac{\partial T}{\partial x} \bigg|_{x=0} = \frac{\bar{u}}{\alpha} (\bar{T}_s - T_0) \frac{\partial \theta}{\partial \xi} \bigg|_{\xi=0} \]  

This can be obtained by differentiating equations A-7 and A-14.

\[ \frac{\partial \theta}{\partial \xi} \bigg|_{\xi=0} = \left( e^{\xi} + \frac{\partial \theta'}{\partial \xi} e^{i\alpha \tau} \right) \bigg|_{\xi=0} = 1 + \frac{\partial \theta'}{\partial \xi} \bigg|_{\xi=0} e^{i\alpha \tau} \]  

Substitution into A-15 gives the temperature gradient

\[ f = \frac{\partial T}{\partial x} \bigg|_{x=0} = \frac{\bar{u}}{\alpha} (\bar{T}_s - T_0) \left( 1 + \left( \theta_s - \frac{iV'}{\Omega} \right) e^{i\alpha \tau} \right) \]  

The surface gradient can be also be written as the sum of mean and oscillatory components. As a result the oscillatory temperature gradient can be written as

\[ \frac{f'}{f} = \theta_s - \frac{iV'}{\Omega} \lambda + \frac{iV'}{\Omega} \]  

Substitution of the definitions for \( V' \) and \( \theta' \) give the temperature gradient at the surface as
Using $T_s$ to non-dimensionalize the temperature instead of $T_s - T_0$ will give the temperature gradient as given by equation A-20

$$q_\prime = \frac{\lambda_p}{\bar{m} C_p \bar{T}_s} \left( \frac{\partial T'}{\partial x} \right) = \lambda \frac{T'}{T_s} + \frac{1}{\lambda} \left( 1 - \frac{T_0}{T_s} \right) \frac{m'}{\bar{m}}$$  \[A-20\]

### A.2 Interface and Gas-Phase Regions

Most gas-phase flame models have used simplified chemical kinetics with species diffusion being entirely neglected or if included has the Lewis number set to one. Thermal conductivity and specific heat are once again considered to be constant. The ideal gas law is assumed to be valid.

The flame model requires the mass flux leaving the surface to be defined in the form of an Arrhenius expression and is given by equation A-21.

$$m = A_s p^n_s \exp \left( \frac{-E_s}{RT_s} \right)$$  \[A-21\]

This mass flux also has a mean and an oscillatory component and can be expressed as A-22

$$\frac{m'}{\bar{m}} = n_s \frac{p'}{\bar{p}} + \frac{E_s}{RT_s} \frac{T'}{T_s} = n_s \frac{p'}{\bar{p}} + E \frac{T'}{T_s}$$  \[A-22\]
Using the assumption that the chemical reaction occurs in a narrow band at the maximum flame temperature (Von Karman flame sheet), the flame speed can be expressed in terms of the flame temperature and pressure.

\[ m = A_f p^{k_1} T_f^{k_2} \exp \left( \frac{-E_f}{2RT_f} \right) \]  

[A-23]

where \( A_f, k_1 \) and \( k_2 \) are constants and \( E_f \) is the activation energy of the gas-phase reaction.

The perturbed form of the equation is given by equation A-24.

\[ \frac{m^*}{m} = k_1 \frac{p^*}{p} + \left( k_2 + \frac{E_f}{2RT_f} \right) \frac{T_f^*}{T_f} = k_1 \frac{p^*}{p} + \left( k_2 + \frac{E_f}{2RT_f} \right) \frac{T_s^*}{T_s} \]  

[A-24]

The heat feedback from the flame can be written as A-25 and A-26

\[ \lambda_g \left( \frac{\partial T}{\partial x} \right) = m(C(T_s - T_f) + Q_g) \]  

[A-25]

\[ q_s = \frac{\lambda_g}{mCT_s} \left( \frac{\partial T}{\partial x} \right) = \frac{m}{m} \left( 1 - \frac{T_f}{T_s} + \frac{Q_g}{CT_s} \right) \]  

[A-26]

and the perturbed form can be written as A-27

\[ q_s^* = \frac{m^*}{m} \left( 1 - \frac{T_f^*}{T_s^*} + \frac{Q_g}{CT_s^*} \right) + \frac{T_s^*}{T_f^*} \frac{T_f^*}{T_s^*} \]  

[A-27]

The relationship between the gas-phase and the condensed phase can be written as

\[ \lambda_g \left( \frac{\partial T}{\partial x} \right) = \lambda_p \left( \frac{\partial T}{\partial x} \right) - mH_p \]  

[A-28]
where \( H_p \) is the surface heat release.

Perturbing equation A-28 and dividing the resulting equation by \( mC_pT_s \) gives A-29

\[
\frac{C}{mC_pT_s} \frac{\lambda_g}{\lambda_p} \left( \frac{\partial T}{\partial x} \right)_+ = \frac{\lambda_p}{mC_pT_s} \left( \frac{\partial T}{\partial x} \right)_- - \frac{H_p}{C_pT_s} \frac{m'}{m} + \left( \frac{C}{C_p} - 1 \right) \frac{T_s'}{T_s}
\]

\[\text{[A-29]}\]

\[
\frac{C}{C_p} q_+ = q_- - H \frac{m'}{m} + \left( \frac{C}{C_p} - 1 \right) \frac{T_s'}{T_s}
\]

We now use the flame sheet equation [A-24], the energy balance equation [A-27] and the mass flux equation [A-22] to obtain an equation of the form given by [A-30].

\[
q_+ = \frac{C_p}{C} X_{T+} \frac{T_s'}{T_s} + \frac{C_p}{C} X_{p+} \frac{p'}{p}
\]

\[\text{[A-30]}\]

where \( X_{T+} \) and \( X_T \) are co-efficients.

The mass flux equation [A-22] is used to eliminate \( m' \) from [A-29] and [A-20] to obtain [A-31].

\[
\frac{C}{C_p} q_+ = q_- + X_T \frac{T_s'}{T_s} + X_p \frac{p'}{p}
\]

\[\text{[A-31]}\]

and

\[
q_- = \left( \lambda + \frac{A}{\lambda} \right) \frac{T_s'}{T_s} + \frac{n_s}{\lambda} \left( 1 - \frac{T_0}{T_s} \right) \frac{p'}{p}
\]

where \( XT = C/C_p - 1 \cdot EH \), \( Xp = -n_sH \), and \( A = E(1-T_0/T_s) \)

Combining equations A-31 and A-30 gives the result for \( T_s' \) in terms of \( p' \).
This can be substituted into A-22 to give a pressure response

$$\frac{T_s'}{T_s} = \frac{X_{p^+} - X_p - \frac{n_s}{\lambda} \left(1 - \frac{T_0}{T_s}\right) p'}{\lambda + A \frac{A}{\lambda} + X_T - X_{T^+}}$$

To ensure correct behavior of the equation as $\Omega \to 0$, $X_T - X_{T^+} = AB - (1 + A)$. This places a restriction on certain quantities introduced in the model for the gas-phase.

The response should also approach the pressure exponent as the frequency approaches zero.

Hence,

$$n = \frac{E(X_{p^+} - X_p) - An_s}{1 + A + AB - (1 + A)} + n_s = \frac{E(X_{p^+} - X_p) - An_s + n_s AB}{AB}$$

This gives

$$E(X_{p^+} - X_p) = nAB + n(A - AB)$$

Substituting A-35 into A-33 gives us
\[ R_p = \left( \frac{m'/m}{p'/p} \right) = \frac{nAB + n_s A - n_s AB - \frac{A n_s}{\lambda} + n_s \left( \frac{\lambda + A}{\lambda} + AB - (1 + A) \right)}{\lambda + \frac{A}{\lambda} + AB - (1 + A)} \]  \hspace{1cm} [A-36]

which reduces to

\[ R_p = \left( \frac{m'/m}{p'/p} \right) = \frac{nAB + n_s (\lambda - 1)}{\lambda + \frac{A}{\lambda} + AB - (1 + A)} \]  \hspace{1cm} [A-37]

with

\[ \lambda = \frac{1}{2} + \frac{\Omega}{2R} + iR \]

\[ R = \frac{1}{2\sqrt{2}} \sqrt{\sqrt{16\Omega^2 + 1} - 1} \]
APPENDIX B

Formulation for Intrinsic Instability of Propellants

A stability plot for propellants is created by setting the denominator in the response equation to zero. This results in equation [1].

\[ \lambda + \frac{A}{\lambda} - (1 + A) + AB = 0 \] [1]

This can also be written as

\[ \lambda(\lambda - 1) + \lambda \cdot A \cdot (B - 1) + A = 0 \] [2]

This gives us a formula for \( \lambda \). We also know that

\[ \lambda \cdot (\lambda - 1) = i\Omega \] [3]


\[ \Omega_r = \pm \frac{1}{2} A(B - 1)[4A - (A - AB + 1)^2]^{1/2} \] [4]

and

\[ \Omega_i = A + \frac{1}{2} A(B - 1)[A - AB + 1] \] [5]

\( \Omega \) appears as the frequency of harmonic time variations. If we consider \( i\Omega \) as a Laplace Transform variable, \( \Omega_i > 0 \) suggests stable transient motions.

The equation can be re-arranged to show that

\( (B + 1) \geq A(B - 1)^2 \) [6]
Appendix C

POWER DETECTOR AND RELATED ELECTRONICS
APPENDIX D

Wiring for Laser-Driven Combustion

Digital Oscilloscope
- Chan A
- Chan B
- Ext. Trig

HP Universal Source
- Chan A
- O/P

Laser Controller
- Gate
- O/P
- ANV/C

PC Board
- Trig From PC

From PC
APPENDIX E

Momentum Imparted By The Laser Photons During Combustion

E.1. Assumptions

Incident laser heat flux = 90 W/cm\(^2\) \[E-1\]

Propellant surface Area = \(\frac{\pi}{4} \cdot \left(\frac{3}{8} \times 2.54\right)^2\) = 2.85 cm\(^2\) \[E-2\]

Laser wavelength = 10.6 \(\mu\)m

The propellant surface is opaque.

E.2. Calculations

The energy imparted by the photons in one second on the propellant surface is given by

\[E = 90 \times 2.85 = 256.52 \text{ J/s} \ [E-3\]

The incident energy on the propellant surface is also given by \[E-4\]

\[E = \frac{\dot{n} h c}{\lambda} \ [E-4\]

where \(\dot{n}\) is the no. of photons incident on the surface per second, \(c\) is the speed of light, \(h\) is Planck’s constant and \(\lambda\) is the wavelength of the incident energy.

As a result,

\[\dot{n} = \frac{E\lambda}{hc} = \frac{256.52 \times 10^{-6}}{6.63 \times 10^{-34} \times 3 \times 10^8} = 128.97 \times 10^{20} \text{ photons / sec} \ [E-5\]

The momentum imparted by the photons = mc.

But,

\[mc^2 = h\nu \ [E-6\]
As a result,

\[
mc = \frac{h\nu}{c} = \frac{h}{\lambda} \quad \text{[E-7]}
\]

The momentum imparted by each photon is given by equation E-8.

\[
mc = 6.63 \times 10^{-34} / 10 \times 10^{-6} = 6.63 \times 10^{-29} \text{ Ns.} \quad \text{[E-8]}
\]

The total momentum rate imparted by the photons is given by E-9

\[
mc = \bar{n} \left( \frac{6.63 \times 10^{-34}}{10 \times 10^{-6}} \right) = 8.55 \times 10^{-7} \text{ N} \quad \text{[E-9]}
\]

The propellant surface is assumed to be opaque and all the photons reflect off the surface.

The total momentum imparted on the surface is thus

\[
F = 2(0.855 \, \mu \text{N}) = 1.71 \, \mu \text{N} \quad \text{[E-10]}
\]
## APPENDIX F

### HMX KINETIC MECHANISM

CHEMKIN INTERPRETER OUTPUT: CHEMKIN-II Version 3.9 Aug. 1994
DOUBLE PRECISION

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<tr>
<th>ELEMENTS</th>
<th>ATOMIC CONSIDERED</th>
<th>WEIGHT</th>
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<td></td>
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<tr>
<td>2. O</td>
<td>15.9994</td>
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<tr>
<td>3. AR</td>
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<tr>
<td>4. C</td>
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<tr>
<td>5. N</td>
<td>14.0067</td>
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<th>S G MOLECULAR</th>
<th>TEMPERATURE</th>
<th>ELEMENT COUNT</th>
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<td>2. H2</td>
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<td>300 5000</td>
<td>2 0 0 0 0</td>
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<td>3. O2</td>
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<td>4. H2O</td>
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<td>5. O</td>
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<td>6. H</td>
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<td>7. OH</td>
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<td>8. HO2</td>
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<td>1 2 0 0 0</td>
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<td>9. H2O2</td>
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<td>10. CH2O</td>
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<td>11. HCO</td>
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<td>12. CO</td>
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<td>17. NO2</td>
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19. NH2      G 0  16.02264   300   5000   2  0  0  0  1
20. NH3      G 0  17.03061   300   5000   3  0  0  0  1
21. NNH      G 0  29.02137   250   4000   1  0  0  0  1
22. HNO      G 0  31.01407   300   5000   1  1  0  0  1
23. HONO     G 0  47.01347   300   5000   1  2  0  0  1
24. HCN      G 0  27.02582   300   5000   1  0  0  1  1
25. HNC      G 0  27.02582   300   5000   1  0  0  1  1
26. N2O      G 0  44.01280   300   5000   0  1  0  0  2
27. CN       G 0  26.01785   300   5000   0  0  0  1  1
28. C2N2     G 0  52.03570   300   5000   0  0  0  2  2
29. NCN      G 0  40.02455   300   4000   0  0  0  1  2
30. NCO      G 0  42.01725   300   5000   0  1  0  1  1
31. CNO      G 0  42.01725   300   4000   0  1  0  1  1
32. HNCO     G 0  43.02522   300   4000   1  1  0  1  1
33. HOCN     G 0  43.02522   300   4000   1  1  0  1  1
34. HCNO     G 0  43.02522   300   4000   1  1  0  1  1
35. NO3      G 0  62.00490   300   5000   0  3  0  0  1
36. HNO3     G 0  63.01287   300   5000   1  3  0  0  1
37. H2CN     G 0  28.03379   300   4000   2  0  0  1  1
38. H2CNH    G 0  29.04176   300   4000   3  0  0  1  1
39. H2CNO    G 0  44.03319   300   4000   2  1  0  1  1
40. H2CNNO   G 0  58.03989   300   4000   2  1  0  1  2
41. H2CNNO2  G 0  74.03929   300   4000   2  2  0  1  2
42. H2COHNNO2 G 0  91.04666   300   4000   3  3  0  1  2
43. HMX      G 0  296.15716   300   4000   8  8  0  4  8
44. HMXR     G 0  250.15166   300   4000   8  6  0  4  7
45. HMXRO    G 0  250.15166   300   4000   8  6  0  4  7

(k = A T**b exp(-E/RT))

REATIONS CONSIDERED

1. H2+M=H+H+M
   H2       Enhanced by  2.500E+00
   H2O      Enhanced by  1.200E+01
   CO       Enhanced by  1.900E+00
   CO2      Enhanced by  3.800E+00
2. O+H2O=OH+OH
   2.97E+06  2.0  13400.0
3. O+H2=H+OH
   5.06E+04  2.7  6290.0
4. O+O+M=O2+M
   6.17E+15  -0.5  0.0
CO Enhanced by 1.900E+00
CO2 Enhanced by 3.800E+00

5. H+O2=O+OH 1.94E+14 0.0 16440.0
6. H+O2(+M)=HO2(+M) 4.52E+13 0.0 0.0
   Low pressure limit: 0.67000E+20 -0.14200E+01 0.00000E+00
   TROE centering: 0.10000E+01 0.10000E-89 0.10000E+91
   H2 Enhanced by 2.500E+00
   H2O Enhanced by 1.200E+01
   CO Enhanced by 1.900E+00
   CO2 Enhanced by 3.800E+00

7. H+O+M=OH+M 4.72E+18 -1.0 0.0
   H2 Enhanced by 2.500E+00
   H2O Enhanced by 1.200E+01
   CO Enhanced by 1.900E+00
   CO2 Enhanced by 3.800E+00

8. OH+H2=H2O+H 2.16E+08 1.5 3430.0
9. OH+H+M=H2O+M 2.21E+22 -2.0 0.0
   H2 Enhanced by 2.500E+00
   H2O Enhanced by 1.200E+01
   CO Enhanced by 1.900E+00
   CO2 Enhanced by 3.800E+00

10. HO2+O=O2+OH 1.75E+13 0.0 -397.0
11. HO2+H=H2+O2 6.62E+13 0.0 2130.0
12. HO2+H=OH+OH 1.69E+14 0.0 874.0
13. HO2+OH=H2O+O2 1.90E+16 -1.0 0.0
14. HO2+HO2=H2O2+O2 4.20E+14 0.0 11980.0
   Declared duplicate reaction...
15. HO2+HO2=H2O2+O2 1.30E+11 0.0 -1629.0
   Declared duplicate reaction...
16. H2O2(+M)=OH+OH(+M) 2.95E+14 0.0 48460.0
   Low pressure limit: 0.12000E+18 0.00000E+00 0.45500E+05
   TROE centering: 0.50000E+00 0.10000E-89 0.10000E+91
17. H2O2+O=OH+HO2 9.64E+06 2.0 3970.0
18. H2O2+H=H2O+OH 1.00E+13 0.0 3590.0
19. H2O2+H=HO2+H2 4.82E+13 0.0 7950.0
20. H2O2+OH=H2O+HO2 1.00E+12 0.0 0.0
   Declared duplicate reaction...
21. H2O2+OH=H2O+HO2 5.80E+14 0.0 9557.0
   Declared duplicate reaction...
22. CH2O+M=HCO+H+M 1.63E+33 -4.1 92550.0
23. CH2O+M=H2+CO+M 8.25E+15 0.0 69540.0
   AR Enhanced by 1.000E+00
24. CH2O+O2=HCO+HO2 2.05E+13 0.0 38920.0
25. CH2O+O=HCO+OH 1.81E+13 0.0 3078.0
26. CH2O+H=HCO+H2 1.26E+08 1.6 2163.0
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<td>27. CH2O+OH=HCO+H2O</td>
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<tr>
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<td>H2O</td>
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<tr>
<td></td>
<td>CO</td>
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<tr>
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<td>CO2</td>
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<td>30. HCO+O2=CO+HO2</td>
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<td>31. HCO+O=CO+OH</td>
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<td>42. N+OH=NO+H</td>
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<tr>
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<td>51. N+HNO=NO2+O</td>
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<td>53. NO+M=N+O+M</td>
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<td>N2</td>
<td>Enhanced by 1.500E+00</td>
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<td></td>
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<tr>
<td>CO2</td>
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<td>54. NO+O(+M)=NO2(+M)</td>
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<td>-0.28700E+01</td>
<td>0.15510E+04</td>
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<td>55. NO+H(+M)=HNO(+M)</td>
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<td>-0.13200E+01</td>
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TROE centering:  0.82000E+00  0.10000E-89  0.10000E+91
56. NO+OH(+M)=HONO(+M)  1.99E+12  -0.1   -721.0
   Low pressure limit:  0.50800E+24  -0.25100E+01  -0.67560E+02
   TROE centering:  0.62000E+00  0.10000E-89  0.10000E+91
H2O   Enhanced by  5.000E+00
57. NO2+NO=NO2+OH  2.11E+12  0.0  -479.0
58. NO+HCO=HNO+CO  7.23E+12  0.0  0.0
59. NO2+O=O2+NO  3.91E+12  0.0  -238.0
60. NO2+O(+M)=NO3(+M)  1.33E+13  0.0  0.0
   Low pressure limit:  0.14900E+29  -0.40800E+01  0.24670E+04
   TROE centering:  0.82600E+00  0.10000E-89  0.31910E+04
61. NO2+H=NO+OH  1.32E+14  0.0  361.6
62. NO2+OH(+M)=HNO3(+M)  2.41E+13  0.0  0.0
   Low pressure limit:  0.64200E+33  -0.54900E+01  0.23500E+04
   TROE centering:  0.83700E+00  0.10000E-89  0.16570E+04
63. NO2+H2O=HONO+HCO  8.02E+02  2.8  13730.0
64. NO2+HCO=CO+HONO  1.24E+23  -3.3  2354.0
65. NO2+HCO=H+CO2+NO  8.39E+15  -0.8  1927.0
66. NO2+CO=CO2+NO  9.03E+13  0.0  33780.0
67. NO2+NO2=NO3+NO  9.64E+09  0.7  20920.0
68. NO2+NO2=2NO+O2  1.63E+12  0.0  26120.0
69. NH+M=N+H+M  2.65E+14  0.0  75510.0
70. NH+O2=HNO+O  3.89E+15  -0.8  1927.0
71. NH+O2=NO+OH  7.60E+10  0.0  1530.0
72. NH+O=NO+H  5.50E+13  0.0  0.0
73. NH+O=N+OH  3.72E+13  0.0  0.0
74. NH+OH=HNO+H  2.00E+13  0.0  0.0
75. NH+OH=N+H2O  5.00E+11  0.5  2000.0
76. NH+N=H2+H  3.00E+13  0.0  0.0
77. NH+O=N2O+H  2.94E+14  -0.4  0.0
   Declared duplicate reaction...
78. NH+H=NO+H  ********  -0.2  0.0
   Declared duplicate reaction...
79. NH+H2=H2+H  2.16E+13  -0.2  0.0
80. NH+NO=NO+HNO  1.00E+11  0.5  4000.0
81. NH+NO2=NO2+OH  1.00E+13  0.0  0.0
82. NH+NH=N2+H+H  5.10E+13  0.0  0.0
83. NH2+O2=HNO+OH  1.78E+12  0.0  14900.0
84. NH2+O=HNO+H  6.63E+14  -0.5  0.0
85. NH2+O=NH+OH  6.75E+12  0.0  0.0
86. NH2+H=NH+H2  6.92E+13  0.0  3650.0
87. NH2+OH=NH+H2O  4.00E+06  2.0  1000.0
88. NH2+N=N2+H2  7.20E+13  0.0  0.0
89. NH2+NO=NNH+OH  2.80E+13  -0.6  0.0
90. NH2+NO=N2+H2O  1.30E+16  -1.3  0.0
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Exponent</th>
<th>Temperature</th>
<th>Energy (Kcal)</th>
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<tbody>
<tr>
<td>91. NH₂⁺NO=N₂+H₂O</td>
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<td>92. NH₂⁺NO=N₂O+H₂</td>
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<td>93. NH₂⁺NO=HNO+NH</td>
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<td>94. NH₂⁺NO₂=N₂O+H₂O</td>
<td>3.28E+18</td>
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<tr>
<td>95. NH₃+M=N₂H+M</td>
<td>2.20E+16</td>
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<td>96. NH₃+O=NH₂+OH</td>
<td>9.40E+06</td>
<td>1.9</td>
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<td>97. NH₃+H=NH₂+H₂</td>
<td>6.40E+05</td>
<td>2.4</td>
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<tr>
<td>98. NH₃+OH=N₂H₂+H₂O</td>
<td>2.04E+06</td>
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<td>99. NH₃+HO₂=NH₂+H₂O</td>
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<td>93470.0</td>
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<tr>
<td>100. NNH⁺M=N₂+H+M</td>
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<td>101. NNH⁺O=N₂O+H</td>
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<td>102. NNH⁺H=N₂+H₂</td>
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<td>103. NNH+OH=N₂O+H₂O</td>
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<td>104. NNH⁺H⁺N₂+H₂</td>
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<td>105. NNH⁺OH=N₂+H₂O</td>
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<td>106. NNH⁺NO=N₂⁺HNO</td>
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<td>107. NNH⁺NH=N₂⁺NH₂</td>
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<td>108. NNH⁺NH₂=N₂⁺NH₃</td>
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<td>109. HNO⁺O₂=NO⁺HO₂</td>
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<tr>
<td>110. HNO⁺O=OH⁺NO</td>
<td>1.81E+13</td>
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<tr>
<td>111. HNO⁺H⁺H₂⁺NO</td>
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<tr>
<td>112. HNO⁺OH⁺H₂O⁺NO</td>
<td>1.00E+13</td>
<td>0.0</td>
<td>993.5</td>
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<tr>
<td>113. HNO⁺HCO=CH₂O⁺NO</td>
<td>6.02E+11</td>
<td>0.0</td>
<td>1987.0</td>
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<tr>
<td>114. HNO⁺NO₂=H₂O⁺NO</td>
<td>2.00E+12</td>
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<td>26000.0</td>
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<tr>
<td>115. HNO⁺NO₂⁺HONO⁺NO</td>
<td>6.02E+11</td>
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<tr>
<td>116. HNO⁺NH₂⁺NO⁺NH₃</td>
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<tr>
<td>117. HNO⁺HNO⁺H₂O⁺NO₂</td>
<td>8.51E+08</td>
<td>0.0</td>
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<tr>
<td>118. HONO⁺O⁺OH⁺NO₂</td>
<td>1.20E+13</td>
<td>0.0</td>
<td>5961.0</td>
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<tr>
<td>119. HONO⁺H⁺H₂⁺NO₂</td>
<td>1.20E+13</td>
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<tr>
<td>120. HONO⁺OH⁺H₂O⁺NO₂</td>
<td>1.26E+10</td>
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<td>121. HCN(+M)=H⁺CN(+M)</td>
<td>8.30E+17</td>
<td>-0.9</td>
<td>123800.0</td>
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</table>

Low pressure limit: 0.35700E+27 -0.26000E+01 0.12490E+06
TROE centering: 0.95700E+00 0.10000E-89 0.83320E+04

122. HCN⁺O⁺CN⁺OH   | 2.70E+09 | 1.6 | 29200.0 |
123. HCN⁺O⁺NH⁺CO   | 3.45E+03 | 2.6 | 4980.0 |
124. HCN⁺O⁺NCO⁺H   | 1.38E+04 | 2.6 | 4980.0 |
125. HCN⁺OH⁺H₂O⁺CN | 3.90E+06 | 1.8 | 10290.0 |
126. HCN⁺OH⁺H⁺HOCN | 5.85E+04 | 2.4 | 12500.0 |
127. HCN⁺OH⁺H⁺HNCO | 1.98E-03 | 4.0 | 1000.0 |
128. HCN⁺OH⁺NH₂⁺CO | 7.83E-04 | 4.0 | 4000.0 |
129. HCN⁺HNC     | 2.06E+14 | -1.1 | 43710.0 |
130. HNC⁺O⁺NH⁺CO  | 2.89E+12 | 0.0 | 0.0 |
131. HNC⁺O⁺H⁺NCO  | 1.60E+01 | 3.1 | -224.0 |
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Temperature</th>
<th>Number of Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNC+OH=HNCO+H</td>
<td>2.80E+13</td>
<td>3700.0</td>
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<tr>
<td>HNC+OH=CN+H2O</td>
<td>1.50E+12</td>
<td>7680.0</td>
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<tr>
<td>HNC+NO2=HNCO+NO</td>
<td>1.00E+12</td>
<td>32000.0</td>
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<tr>
<td>HNC+CN=C2N2+H</td>
<td>1.00E+13</td>
<td>0.00</td>
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<tr>
<td>N2O(+M)=N2+O(+M)</td>
<td>7.91E+10</td>
<td>56020.0</td>
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</table>

Low pressure limit: 0.91300E+15 0.00000E+00 0.57690E+05

- H2O  Enhanced by 7.500E+00
- NO   Enhanced by 2.000E+00
- CO   Enhanced by 2.000E+00
- CO2  Enhanced by 3.000E+00
- HCN  Enhanced by 3.000E+00

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Temperature</th>
<th>Number of Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2O+O=O2+N2</td>
<td>1.00E+14</td>
<td>28000.0</td>
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<tr>
<td>N2O+O=2NO</td>
<td>1.00E+14</td>
<td>28000.0</td>
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</table>

Declared duplicate reaction...

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Temperature</th>
<th>Number of Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2O+H=N2+OH</td>
<td>2.53E+10</td>
<td>4550.0</td>
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<tr>
<td>N2O+H=N2+OH</td>
<td>2.23E+14</td>
<td>16750.0</td>
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Declared duplicate reaction...

<table>
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<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Temperature</th>
<th>Number of Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2O+OH=HO2+N2</td>
<td>2.00E+12</td>
<td>40000.0</td>
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<tr>
<td>N2O+CO=NO2+CO2</td>
<td>5.01E+13</td>
<td>440000.0</td>
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<tr>
<td>CN+H2=H+HCN</td>
<td>5.50E+02</td>
<td>-223.0</td>
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<tr>
<td>CN+O2=NCO+O</td>
<td>7.50E+12</td>
<td>-389.0</td>
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<tr>
<td>CN+O=CO+N</td>
<td>1.80E+13</td>
<td>0.00</td>
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</tr>
<tr>
<td>CN+OH=NCO+H</td>
<td>4.22E+13</td>
<td>0.00</td>
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<tr>
<td>CN+CH2O=HCN+HCO</td>
<td>4.22E+13</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>CN+HCO=HCN+CO</td>
<td>6.02E+13</td>
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<td>0.00</td>
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<tr>
<td>CN+CO2=CO+NCO</td>
<td>3.67E+06</td>
<td>26900.0</td>
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<tr>
<td>CN+NO=HCN+N</td>
<td>9.64E+13</td>
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<tr>
<td>CN+NO2=NCO+NO</td>
<td>1.59E+13</td>
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<tr>
<td>CN+HNO=HCN+NO</td>
<td>1.81E+13</td>
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<td>0.00</td>
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<tr>
<td>CN+HONO=HCN+NO2</td>
<td>1.20E+13</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>CN+HCN=H+C2N2</td>
<td>1.21E+07</td>
<td>1530.0</td>
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<tr>
<td>CN+N2O=NCN+NO</td>
<td>3.85E+03</td>
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<tr>
<td>CN+CN(+M)=C2N2(+M)</td>
<td>5.66E+12</td>
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Low pressure limit: 0.34200E+26 -0.26100E+01 0.00000E+00

TROE centering: 0.50000E+00 0.10000E-89 0.10000E+91

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Temperature</th>
<th>Number of Steps</th>
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<tbody>
<tr>
<td>C2N2+O=NCO+CN</td>
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<tr>
<td>C2N2+OH=HOCN+CN</td>
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<tr>
<td>NCN+O2=NO+NCO</td>
<td>1.00E+14</td>
<td>0.00</td>
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<tr>
<td>NCN+O=CN+NO</td>
<td>1.00E+14</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>NCN+H=HCN+N</td>
<td>1.00E+14</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>NCN+OH=HCN+NO</td>
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<td>NCO+M=N+CO+M</td>
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N2  Enhanced by 1.500E+00

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<th>Temperature</th>
<th>Number of Steps</th>
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<tbody>
<tr>
<td>NCO+H2=HNCO+H</td>
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<tr>
<td>NCO+O2=NO+CO2</td>
<td>2.00E+12</td>
<td>20000.0</td>
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<tr>
<td>Reaction</td>
<td>Rate Constant (s^-1)</td>
<td>Pre-Exponential (cm^3 molecule^-1 s^-1)</td>
<td>Temperature (K)</td>
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<td>----------</td>
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<tr>
<td>NCO + O = CO + NO</td>
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<tr>
<td>NCO + H = NH + CO</td>
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<tr>
<td>NCO + OH = NO + CO + H</td>
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<tr>
<td>NCO + OH = NO + HCO</td>
<td>5.00E+12</td>
<td>0.0</td>
<td>15000.0</td>
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<tr>
<td>NCO + CH2O = HNCO + HCO</td>
<td>6.02E+12</td>
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<tr>
<td>NCO + HCO = HNCO + CO</td>
<td>3.61E+13</td>
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<td>NCO + N = N2 + CO</td>
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<tr>
<td>NCO + NO = N2O + CO</td>
<td>6.20E+17</td>
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<tr>
<td>NCO + NO = CO2 + N2</td>
<td>7.80E+17</td>
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<td>763.0</td>
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<tr>
<td>NCO + NO2 = CO + 2NO</td>
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<tr>
<td>NCO + NO2 = CO2 + N2O</td>
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<tr>
<td>NCO + HNO = HNCO + NO</td>
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<tr>
<td>NCO + HONO = HNCO + NO2</td>
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<tr>
<td>NCO + N2O = N2 + CO + NO</td>
<td>9.03E+13</td>
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<td>27820.0</td>
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<tr>
<td>NCO + CN = NCN + CO</td>
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<tr>
<td>NCO + NCO = N2 + 2CO</td>
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<tr>
<td>CNO + O = CO + NO</td>
<td>1.00E+13</td>
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<td>0.0</td>
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<tr>
<td>CNO + NO2 = CO + 2NO</td>
<td>1.00E+13</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>CNO + N2O = N2 + NO + CO</td>
<td>1.00E+12</td>
<td>0.0</td>
<td>15000.0</td>
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<tr>
<td>HNCO (+M) = NH + CO (+M)</td>
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<tr>
<td>NCO + O2 = HNCO + CO2</td>
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<tr>
<td>NCO + N2O = N2 + NO + CO</td>
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<td>0.0</td>
<td>27820.0</td>
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<tr>
<td>NCO + CN = NCN + CO</td>
<td>1.81E+13</td>
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<tr>
<td>NCO + N2O = N2 + CO + NO</td>
<td>1.00E+13</td>
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<tr>
<td>CNO + O = CO + NO</td>
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<td>CNO + NO2 = CO + 2NO</td>
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<td>CNO + N2O = N2 + CO + NO</td>
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<td>HNCO (+M) = NH + CO (+M)</td>
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<td>HOCN = NH + CO2</td>
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<td>HCNO + O2 = NCO + H2O2</td>
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<td>HCNO + NH2 = NHCN + H2O</td>
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<td>-------</td>
<td>------</td>
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<tr>
<td>209</td>
<td>$\text{H}_2\text{CN} + \text{HONO} = \text{H}_2\text{CNH} + \text{NO}_2$</td>
<td>$1.00 \times 10^{11}$</td>
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<td>$\text{H}_2\text{CNH} + \text{N}_2\text{O} = \text{H}_2\text{CNO} + \text{N}_2$</td>
<td>$1.00 \times 10^{11}$</td>
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<td>$1.00 \times 10^{13}$</td>
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<td>212</td>
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<td>0.15</td>
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<td>220</td>
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<td>222</td>
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<td>223</td>
<td>$\text{H}_2\text{CNO} + \text{NO}_2 = \text{CH}_2\text{O} + \text{N}_2\text{O} + \text{NO}$</td>
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<td>$\text{H}_2\text{CNO} + \text{OH} = \text{CH}_2\text{O} + \text{N}_2\text{O} + \text{OH}$</td>
<td>$1.00 \times 10^{13}$</td>
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<td>227</td>
<td>$\text{HMX} + \text{M} = \text{HMXR} + \text{NO}_2 + \text{M}$</td>
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<td>$\text{HMX} + \text{H} = \text{HMXR} + \text{HONO}$</td>
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<td>$\text{HMX} + \text{OH} = \text{3H}_2\text{CNO} + \text{H}_2\text{COHNNO}_2$</td>
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<td>230</td>
<td>$\text{H}_2\text{COHNNO}_2 = \text{HCN} + \text{NO}_2 + \text{H}_2\text{O}$</td>
<td>$1.00 \times 10^{16}$</td>
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<td>$\text{HMXR} + \text{M} = \text{HMXRO} + \text{M}$</td>
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<td>232</td>
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<td>$1.00 \times 10^{16}$</td>
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<td>Low pressure limit: $0.76900 \times 10^{17}$</td>
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<td>0.18</td>
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</table>

**NOTE:** A units mole-cm-sec-K, E units cal/mole
## APPENDIX G

### AP/HTPB KINETIC MECHANISM

CHEMKIN INTERPRETER OUTPUT: CHEMKIN-II Version 3.9  Aug. 1994  
DOUBLE PRECISION

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<td>4. N</td>
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<th>MOLECULAR WEIGHT</th>
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<th>A</th>
<th>b</th>
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<td>1. HCLO4=CLO3+OH</td>
<td>(k = A T^b \exp(-E/RT))</td>
<td>1.00E+14</td>
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<td>3. HCLO4+HCO=CLO3+CO+H2O</td>
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<td>4. HCLO4+HCO=CLO2+CO2+H2O</td>
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<td>5. CLO3=CLO+O2</td>
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<td>7. CLO+NO=CL+NO2</td>
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<td>8. CLOH+CLO=CL2+HO2</td>
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<td>10. HCL+OH=CL+H2O</td>
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<td>11. CL2+H=HCL+CL</td>
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22. NO+H+M=HNO+M                                   3.20E+12    0.0     -600.0
23. N2+HO2=HNO+NO                                  8.00E+10    0.5    41800.0
24. NO+HO2=NO2+OH                                  3.00E+12    0.5     1800.0
25. NO2+H=NO+OH                                    5.00E+14    0.0     1740.0
26. H2+OH=H2O+H                                    1.00E+08    1.6     3290.0
27. CH2CO+OH=CH2O+HCO                              2.82E+14    0.0        0.0
28. CH2CO+NO2=CH2O+CO+NO                           1.00E+13    0.0     6000.0
29. C2H3+O2=CH2O+HCO                               6.00E+13    0.0        0.0
30. C2H2+H(+M)=C2H3(+M)                            5.60E+12    0.0     2400.0

Low pressure limit:  0.12000E+43 -0.76200E+01  0.69700E+04

31. C2H2+OH=CH3+CO                                 2.00E+12    0.0     7000.0
32. H2+CO(+M)=CH3+HCO                              4.30E+07    1.5    79600.0

Low pressure limit:  0.50700E+28 -0.34200E+01  0.84350E+05

33. CH4+CL=CH3+HCL                                 2.50E+13    0.0     3830.0
34. CH4+CLO=CH3+CLOH                                6.00E+11    0.5     5700.0
35. CH4+H=CH3+H2                                    2.20E+04    3.0     8520.0
36. CH4+OH=CH3+H2O                                 1.02E+07    2.0     1900.0
37. CH3+H(+M)=CH4(+M)                              2.50E+16   -0.8        0.0

Low pressure limit:  0.27000E+39 -0.63000E+01  0.31000E+04

38. HCO+M=CO+H+M                                   2.50E+14    0.0     16800.0
39. HCN+OH=NH2+CO                                   2.00E+11    0.0        0.0
40. CO+OH=CO2+H                                      4.40E+06    1.5    -740.0
41. CO+CLO=CO2+CL                                   3.00E+12    0.0     1000.0
42. CO+CLO2=CO2+CLO                                  1.00E+10    0.0        0.0
43. C2H4+OH=H2O+C2H3                                3.60E+06    2.0    2500.0
44. C4H6+OH=2C2H2+H2O+H                             5.00E+12    0.7     1100.0
45. C4H6+CLO=2C2H2+CLOH+H                           5.00E+12    0.5     6400.0
46. C4H6+CL=2C2H2+HCL+H                             6.75E+12    0.5     100.0
47. H+O2=O+OH                                       8.30E+13    0.0    14413.0
48. C2H2+O=CH2+CO                                   1.02E+07    2.0     1900.0
49. CH2+H2=CH3+H                                   5.00E+05    2.0     7230.0
50. CH2+H(+M)=CH3(+M)                              2.50E+16   -0.8        0.0

Low pressure limit:  0.70000E+51 -0.93100E+01  0.99860E+05

51. CH4+O=CH3+OH                                    1.02E+09    1.5     600.0
52. CH3+O=CH2O+H                                      8.43E+13    0.0        0.0
53. CH2+O=H+HCO                                     8.00E+13    0.0        0.0
54. CH3+O2=OH+CH2O                                  3.60E+10    0.0     8940.0
55. OH+CH3=CH2+H2O                                  5.60E+07    1.6     5420.0
56. OH+CH2=H+CH2O                                   2.00E+13    0.0        0.0
57. CH2+O2=OH+HCO                                   1.32E+13    0.0     1500.0
58. C2H4+O2=2CO+2H2                                 1.80E+14    0.0     35500.0
59. O2+HNO=NO+HO2                                   1.00E+13    0.0     13000.0
60. NH2+NO2=2HNO                                    2.00E+12    0.0        0.0
61. NH2+CLO=HNO+HCL                                 2.50E+12    0.0        0.0
62. H+CL+M=HCL+M                                    5.30E+21   -2.0   -2000.0
63. CL+HO2=CLO+OH 2.47E+13 0.0 894.0
64. CLO+O=CL+O2 9.70E+12 0.0 507.0
65. HCL+H=H2+CL 2.30E+13 0.0 3500.0
66. HCL+O=OH+CL 5.24E+12 0.0 6400.0
67. CL2+O=CL+CLO 2.51E+12 0.0 2720.0
68. N2O(+M)=N2+O(+M) 1.30E+11 0.0 59620.0

Low pressure limit: 0.62000E+15 0.00000E+00 0.56100E+05

69. N2O+OH=N2+HO2 2.00E+12 0.0 21060.0
70. N2O+O=NO+NO 2.90E+13 0.0 23150.0
71. N2O+O=N2+O2 1.40E+12 0.0 10810.0
72. N2O+H=N2+OH 4.40E+12 0.0 18880.0

NOTE: A units mole-cm-sec-K, E units cal/mole
VITA

Gautam Narendra Kudva was born in Bangalore, India on June 2\textsuperscript{nd} 1973. He received a Bachelor of engineering degree in Mechanical Engineering from the University of Pune, India in 1994. He began in graduate study at The Pennsylvania State University in August 1994. He has focused on analysis of steady and unsteady combustion behavior in rocket and gun propellants. He married Michelle Chatfield in May 1997. He is a member of the American Institute of Astronautics and Aeronautics.