CHARACTERIZATION OF THERMAL RADIATION FROM A PLASMA JET
AND RADIATIVE PYROLYSIS OF DOUBLE-BASE PROPELLANTS

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by
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ABSTRACT

The present research experimentally investigates radiative heat transfer from a hydrocarbon capillary-sustained plasma jet, and the role of the radiation during the plasma-propellant interaction. The plasma jet is initiated by exploding a thin metallic trigger wire (~3.6mg) through a high-voltage electrical pulse. The exploding wire ablates the hydrocarbon capillary, forms a high-temperature, high-pressure electrothermal-chemical (ETC) plasma that emerges in the open-air environment as an underexpanded, supersonic jet. The ETC plasma jet is allowed to impinge over a stagnation plate that holds a variety of diagnostic tools as well as the propellant samples.

The overall objective of this research is to augment the present understanding of the thermophysical and chemical processes involved in the ETC ignition of solid propellants. The particular focus is to deduce the transient variation in radiative heat flux, stagnation pressure, electrical parameters, and plasma jet structure with different capillary and trigger-wire materials, plasma energy levels, and plasma exit port to stagnation plate distance. The effects of trigger-wire mass and capillary diameter are also examined. To understand the role of radiation during ETC ignition, double-base JA2 propellants are exposed to ETC plasma radiation. A variety of measurements are conducted to analyze the gas-phase products generated during the radiative pyrolysis of JA2. These include measurement of transient variation in gas-phase temperature and pressure, identification of gas-phase species, and estimation of species relative mole fractions. To further elucidate the radiative pyrolysis studies of JA2, confined rapid thermolysis of JA2 propellants are also conducted.
A considerable effort is employed to develop thin-film platinum heat flux gages, electrical circuitry, and the corresponding inverse data reduction techniques to estimate the transient radiant heat flux from ETC plasma. A high-speed CCD camera captures the side-view images of the plasma jet. Photodiodes, placed below the plasma jet, identifies the plasma emergence from the exit port and the plasma impingement on the stagnation plate. K-type thermocouples (12\(\mu\)m diameter) are used to measure the gas-phase temperature during radiative pyrolysis of JA2.

Results suggest that the instantaneous value of the transient absorbed radiant heat flux is quite high (~10\(^3\) MW/m\(^2\)), and that the contribution from the UV wavelength region dominates over the visible and IR regions. It is also observed that the radiant flux is material dependent, and that for a given electrical energy level and pulse duration, higher ablation typically leads to lower radiant flux as well as higher stagnation pressure. Radiative pyrolysis of JA2 within a constant-volume chamber suggests that, for moderate plasma energy levels, radiative heating alone may produce a high temperature and pressure of the products evolved into the gas-phase region, but cannot ignite the propellant. Additionally, species produced during radiative pyrolysis of JA2 are found to be different from that generated during standard thermolysis experiments, but that may be expected due to differences in temperatures and pressures in the two experiments. It is possible that the UV radiation from the ETC plasma photolyzes the oxidizers (such as NO\(_2\)), and thus reduces the chemical activity of decomposition products, prohibiting ignition of JA2.
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NOMENCLATURE

\( c \) = specific heat, \( \text{J/kg K} \)

\( d \) = domain length in \( y \) direction, m

\( e \) = relative difference between 1- and 2-D estimations

\( h_{fg} \) = enthalpy of vaporization, \( \text{J/kg} \)

\( I \) = current, \( \text{A} \)

\( I_{\text{pot}} \) = ionization potential, \( \text{eV} \)

\( j \) = iteration number

\( k \) = conductivity, \( \text{W/m K} \)

\( l \) = domain length in \( x \) direction, m

\( q'' \) = heat flux, \( \text{W/m}^2 \)

\( t \) = time, \( \text{s} \)

\( T \) = temperature, \( \text{K} \)

\( T_{\text{boil}} \) = boiling point, \( \text{K} \)

\( T_{\text{dec}} \) = decomposition temperature, \( \text{K} \)

\( T_{\text{melt}} \) = melting point, \( \text{K} \)

\( V \) = voltage, \( \text{volt} \)

\( V(t) \) = voltage at time \( t \), \( \text{volt} \)

\( w \) = half-width of gage, \( \text{m} \)

\( x, y \) = Cartesian coordinate direction, \( \text{m} \)

\( Y \) = measured temperature, \( \text{K} \)
\( \alpha \) = thermal diffusivity, \( m^2/s \)

\( \beta \) = temperature coefficient of resistivity, \( 1/K \)

\( \Gamma \) = confidence interval

\( \theta \) = non-dimensional temperature

\( \rho \) = density, \( kg/m^3 \)

\( \tau \) = non-dimensional time (Fourier number)

\( \sigma \) = standard deviation

**Superscripts**

\( j \) = iteration number

\( * \) = non-dimensional

**Subscripts**

\( ave \) = average

\( f \) = final

\( max \) = maximum

\( ref \) = ambient
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Chapter 1

INTRODUCTION

1.1 Background

Propulsive power in a traditional large-caliber gun relies on chemical energy released during combustion of an energetic propellant. Muzzle velocity of projectile in a typical large caliber gun is less than 2km/s and is limited by the sonic speed of the combustion products [1]. It has been challenging to further increase the muzzle velocity in existing gun systems by either modifying the charge design, using different propellant ingredients, or incorporating layered propellants. To use different ingredients, a wide variety of safety requirements must be met, and to date very few newly synthesized ingredients have been incorporated in gun systems in the U.S. Layered propellants, which may offer the opportunity to tailor the burn rate during the ballistic curve, have not been possible due to molecular migration issues. Thus other methods have been sought to improve the performance.

Electromagnetic (EM), and electrothermal (ET) guns, which utilize electrical energy instead of chemical energy of a propellant, may not only enhance the muzzle velocity but also reduce “ignition” delays and “ignition” variability [2-5]. However, complicated electrical systems, as well as the low energy density of typical electrical systems (~J/g) compared to solid propellants (~kJ/g) appear to have hindered further development of EM and ET technologies. Electrothermal-chemical (ETC) systems
combine high-energy density of conventional chemical ignition with high controllability of ET technology, and thus offer an opportunity to develop an optimized ignition system for the next generation of guns.

Unlike conventional ignition, ETC technology uses an electrically initiated, ablation-sustained plasma jet to ignite the propellant. Essential components of a conceptual ETC system are shown in Fig. 1.1. A typical ETC system uses a high-voltage electrical pulse to explode a thin metallic trigger wire, placed within a hydrocarbon capillary. The wire explosion creates a metal-vapor plasma, sustained by the capillary ablation. Resulting ablation-sustained plasma jet attains a temperature ranging from about 10,000 to 30,000K, and an electron number density of $10^{23} - 10^{26} \text{m}^{-3}$. The plasma jet then emerges from the capillary as a high-temperature, high-pressure, supersonic...
underexpanded jet that impinges directly over the propellant to initiate the combustion. Initial experiments shows that, unlike conventional guns, muzzle velocity of ETC guns can reach up to 7km/s. Additionally, compared to conventional chemical ignition, ETC technology provides reproducible gun performance, energy efficient ignition with reduced delay and jitter, as well as a capability for temperature compensation [6-11].

During the last several decades, considerable research was conducted to identify the advantages of ETC ignition systems. Excellent reviews of these studies are also available [1, 12-16]. While the benefits of ETC ignition are now well documented, the thermophysical and chemical mechanisms responsible for this improved performance are yet to be deciphered. It is generally agreed that the plasma-propellant interaction during ETC ignition involves a combination of several complex thermochemical processes. Due to high temperature, pressure, and velocity, ETC plasma may act as a high convective-radiative source that can distribute energy more evenly and rapidly within the propellant charge. High stagnation pressure can produce micro cracks on the propellant surface, thereby increasing the effective reaction area. Additionally ETC plasma can act as a source of highly reactive radicals and electrons, providing efficient chemical reactions. Efficient design and optimization of an ETC ignition system requires quantitative understanding of the plasma-propellant interaction mechanisms as well as the thermophysics of the ablative plasma jet.

In recent years, considerable efforts were employed to understand the mechanism of ETC ignition. Experiments measured the temperature, and pressure as well as identified the essential gas dynamic features of the plasma jet [10, 17-18]. Experiments are also conducted to outline the performance of different propellants in ETC guns [19-
Unfortunately, experimental investigations in an ETC plasma environment are quite challenging for several reasons. ETC plasma experiments involve measurements in a high-pressure, high-temperature, highly transient environment. Additionally, during ETC ignition experiments, several kJ of electrical energy is discharged within few microseconds, inducing high electromagnetic noise in various transducers and data acquisition systems [18]. Numerical simulation of ETC propulsion is also very challenging. A realistic simulation of ETC plasma requires a numerical model that combines supersonic, turbulent flow of non-ideal, chemically reacting plasma jet. Non-equilibrium thermodynamic effects as well as thermal radiation are also important in ETC plasma simulation. Development of a theoretical model of such complexity can be prohibitively difficult, not to mention the computational resources required for a realistic prediction. Several numerical models of varying complexities are proposed to augment the present understanding of ETC ignition [11, 22-36]. Assumptions, simplifications, and applicability of these models, however, require independent experimental verification.

Measurement or computation of radiant heat flux from ETC plasma, understanding the temporal and spectral variation of the plasma radiation, as well as identifying the role of radiant heating during plasma ignition are some of the serious issues in ETC plasma research. As the temperature of the ETC plasma is quite high, it is intuitive that the radiant flux also will be significant. While limited information is available from optical measurements, severe electrical noise hindered all previous attempts to measure the transient radiant heat flux [18, 37-38]. Additionally, an existing numerical model, available in the open literature, is not capable of simulating the combined effects of thermal radiation, turbulent and high-temperature gas dynamics as
well as detailed chemical kinetics. The effect of radiative heating is often neglected in numerical models, or modeled in a very simplified way. Further experiments on ETC radiation are, therefore, necessary to understand the thermophysics of plasma radiation as well as to provide experimental data for numerical model validation.

There are two primary objectives of the present research: 1) to quantify the transient variation of thermal radiation from ETC plasma, and 2) to understand the role of radiative heat transfer during ETC ignition. During the course of this research, transient radiant heat fluxes are measured for a wide range of plasma energy level as well as capillary and trigger wire materials. Thin-film heat-flux gages and the corresponding data-reduction schemes have been developed for pursuing this investigation. Transient stagnation pressure, electrical and ablation characteristics are also measured. Additionally, double-base JA2 propellants were exposed to ETC radiation, and the pyrolysis products were identified using Fourier transform infrared (FTIR) spectroscopy and time-of-flight (ToF) mass spectrometry. To understand the radiative pyrolysis more clearly, confined rapid thermolysis of JA2 samples are also conducted.

1.2 Overview of the Thesis

This thesis is broadly divided into eight chapters. The background of this research is described in Chapter 1. Chapter 2 contains the initial studies on radiant heat flux measurements. Material dependent behavior of ETC plasma radiation is discussed in Chapter 3. Chapter 4 describes the development of a new heat flux gage and data reduction technique. Parametric studies on ETC plasma radiation are covered in Chapter
5. The behavior of standard double-base propellants under confined rapid thermolysis is discussed in Chapter 6. Chapter 7 outlines the radiative pyrolysis of JA2 propellant. Finally, the understanding on radiative heat transfer from ETC plasma is summarized in Chapter 8. To improve the readability of the thesis, Chapters 2 to 7 are written in the form of individual papers, and any one of these chapters can be studied individually.

1.3 References


Chapter 2

INVESTIGATION OF RADIATIVE HEAT TRANSFER FROM ETC PLASMA

2.1 Abstract

The objective this chapter is to develop a better understanding of transient behavior of radiative heat transfer from a plasma jet. The plasma generation occurred within a 3.2 mm diameter and 26 mm long polyethylene capillary. Due to its high-temperature and high-pressure, the plasma evolved from the capillary into an ambient air environment as an underexpanded supersonic jet that interacted with a stagnation plate. Various diagnostic techniques were used. They include heat flux and pressure gauges mounted on the stagnation plate, heat flux and silicon photodiodes mounted below the plasma jet, as well as current transducers interfaced with the electrical circuit. The heat flux gauges were manufactured via sputtering, and calibrated using a standard convection oven. A fused-silica window, placed about 1 mm above the gauges, ensured that only the radiative heat flux transmitted by the window was deduced. The row of heat flux gauges mounted below the plasma provided an assessment of the fraction of the radiative heat flux transmitted by the fused silica window. The results show that the peak of emitted radiant flux occurs immediately after the peak of the discharge of electrical energy, which usually occurred a relatively long time prior to arrival of the precursor shock on the stagnation plate.
2.2 Introduction

The use of a high temperature and high pressure plasma for ignition of solid propellants has recently received considerable attention [1-8]. The high temperatures and pressures produce a complex interaction between the plasma and the propellant, as well as involves several modes of energy transport. First, the characteristic velocities and thermal conductivity of the plasma are large, thereby producing high convective heat transfer coefficients. Second, the plasma contains electrons, ions, atoms and low molecular weight species from the ablation of capillary and electrodes that contribute significantly to the thermal radiation in the UV-visible wavelength range. Third, as the plasma cools, in particular in the interaction region near the propellant’s surface, heat is released from recombination reactions among electrons, ions, atoms and low molecular weight species. Finally, chemical reactions between products from the solid propellant and products from the plasma may enhance the chemical reactions, thereby producing reduced ignition delays compared to conventional ignition systems. However, there are few studies available in the literatures that have attempted to characterize heat transfer rates from plasmas generated by capillary discharges.

Information about average heat flux rates to plasma-exposed surfaces were deduced by Williams and White [9]. They allowed plasma impingement on a black carbon coated thin copper plate. The temperature history on the back side of the plate was captured using an unfiltered infrared camera. An inverse analysis was utilized to deduce average heat flux rates from the temperature data. This work served as a refinement of the earlier effort by White et al. [10], in which thermocouples were used on the back side
of the copper plate. Infrared photography was utilized rather than thermocouples, since the electrical noise likely caused by rapidly varying electromagnetic fields was significant.

Taylor [11-12] performed radiative heat flux measurements on plasmas emerging from a long capillary into stagnant air at 1 atm. The experimental configuration was similar to the one used by Hankins and Mann [13] and Hankins et al. [14-15]. A polyethylene capillary of about 175 mm in length was employed, coupled with very large input energy levels of 40 kJ. The copper initiation wire was 1 mm in diameter, which is significant. Time-resolved spectroscopy was utilized, covering the wavelength range from 258 to 892 nm. The spectrometer was calibrated using a standard deuterium lamp for wavelengths between 258 and 400 nm, and a tungsten lamp for 336 to 892 nm. Measurements at the exit port suggested that the radiant heat flux levels are much lower than expected, with maximum brightness temperatures of 14,500K. In view of the deduced low radiant heat flux levels, Taylor [16] suggested that metal vapor condensation, with its concomitant release of latent heat, contributed significantly to the short ignition delays. In addition, Proud and Bourne [17] examined plasma injection after ignition of a nitroguanidine-based propellant; a 60% burn rate enhancement was observed but its cause was not explained.

In subsequent works, Taylor measured the radiative heat flux in plasma-propellant interactions using time-resolved UV/visible spectroscopy [18-19]. Measurements covered a wavelength range from 369 nm to 1027 nm, and spectra were acquired at a time resolution of about 50 µs. Experiments were conducted in two different
configurations. Aluminum and copper wires of 0.5 mm diameter were used as plasma initiators. In the first case, the exploding wire was placed coaxially with an open-ended propellant cylinder. The second test case was conducted in a 400 cm$^3$ closed chamber by placing the propellant at one end plate and a capillary plasma generator at the opposite end plate. A conventional ignition system using a puffer bag was also tested in the second configuration. Using a translucent propellant, it was concluded that the damage sustained in the propellant’s internal grain structure was not attributed to the radiative heat flux. The type of material used for the plasma initiation wire played an important role in the damage of the propellant’s grain structure.

Gruber et al. [20] and Kappen and Bauder [21-22] developed a model of spectral radiative heat transfer from high-temperature and high-pressure plasmas. Based on the assumption of local thermodynamic equilibrium, that is, translational, rotational and vibrational temperatures are equal, the numerical framework can readily compute the radiation heat transfer with input of plasma properties, including temperature and partial pressure of a wide variety of ions, atoms, diatomic and triatomic species. It appears that carefully conducted emission measurements from various hydrocarbon plasmas could yield important information about species present and line-of-sight temperatures at various positions using the developed code. For such an analysis, calibration of the acquired spectra is not needed. However, to deduce the total radiant heat flux, calibration is needed.

The above discussion reveals a limited understanding of the various heat transfer modes from capillary discharges. The objective of this study is two-fold: 1) to describe a
heat flux gauge design with a high frequency response, and 2) to quantify the transient variation of the radiative heat flux from a plasma produced by a capillary discharge.

2.3 Experimental Apparatus and Approach

2.3.1 Plasma Generator

A schematic of the electrical circuit and plasma chamber with gauge locations is shown in Fig. 2.1. The pulse-forming network (PFN) is mainly comprised of an energy storage component that consists of two high-voltage, fast-discharge capacitors connected in parallel to yield a total capacitance of 192 µF, pulse-shaping components including a 20 µH inductor and a crowbar diode, a floating high-voltage mercury switch (ignitron), as well as a circuit for triggering the ignitron. The capacitors can be charged up to 10 kV to yield a maximum energy storage of 9.6 kJ. The plasma chamber consists of a capillary, a fine metallic wire, electrodes, and other non-conducting housing hardware. The capillary is made of high-density polyethylene, which is machined to have a bore length of 26 mm and a typical diameter of 3.2 mm. Located at each end of the capillary is an electrode made of elkonite (30% Cu, 70% W), which is resistant to material erosion. A fine copper wire of 0.16 mm diameter, which runs through the capillary and connects the electrodes, serves as the discharge initiator. After being formed immediately upon triggering the ignitron, the plasma flows through a nozzle that has dimensions of 3.2 mm (orifice diameter) and 26 mm (length) into the ambient open-air environment. The nozzle is designed to have this length simply for accommodating the relatively large dimensions of
the plasma chamber, which is needed to maintain its structural integrity in case of anomalous pressure excursions.

Figure 2.1 Schematic of electrical circuit, plasma chamber, and location of stagnation plate.

Figure 2.2 shows the locations of the various gauges used in the experiment. Heat flux gauges are placed at two different locations. One configuration corresponds to measurements at the location of the pressure gauges on the stagnation plate, to yield the maximum heat flux rates. In this configuration, the gauges are covered with two fused silica windows (S1-UV, ESCO Products): one sacrificial 1.59 mm thick and a second 4.76 mm thick. The second row of heat flux gauges is located below the plasma. It is used to determine the extent of transmission by the fused silica window. The fused silica window is needed for two reasons. First, the goal is to allow a determination of the radiative heat flux as opposed to the total heat flux (radiative, convective and heat release
from recombination reactions). The use of fused silica windows allows the former but prevents the latter two energy exchange mechanisms. Second, some ionic species or charged particles arrive at the plasma-solid interface and tend to produce significant electrical noise.

Figure 2.2. Schematic of pressure transducer, heat flux gauge and diode locations with respect to plasma emergence from capillary.

The diodes are used to determine plasma emergence (left diode) and plasma arrival (right diode). Diode 1 (Si) is located directly below the plasma exit port. Diode 2 is also located below the plasma flow, but is placed at a distance of 48 mm from Diode 1. Both diodes thus have a side view of the plasma; their spectral range covers 300 to 900 nm. The diodes view the plasma through a 6 mm long, 0.71 mm diameter hole, and have a response time <10 ns. The incident power on the diodes is thus reduced significantly.
Kistler pressure transducers were used (model 211B3) having a measurement range of 0-34.47 bar. To avoid direct impact of the plasma on the transducers, the sensing area of the pressure transducers were covered with a thin tape. Pearson coils are used to deduce the instantaneous current and voltage across the plasma. Data acquisition was performed at 1 MHz using 12-bit transient recorders from Nicolet MP120/150, whose minimum bandwidth is 400 kHz.

Side-view images of the plasma were taken using a Cordin model 222-B CCD camera. It consists of 8 CCDs and is capable of acquiring 16 images, each with a resolution of 1,300 by 1,030 pixels, a 10-bit dynamic range, and exposure gates down to 10 ns. The first and last 8 images can be acquired at a speed of up to $10^8$ pictures per second, but these two sets of 8 images are interrupted by a delay of several microseconds for transfer of the charge.

### 2.3.2 Heat Flux Gage Design

A thin-film sensor and circuitry were designed and manufactured for deducing the transient variation of the radiative heat flux. The principle of its operation is that a constant current flows through a thin metal layer whose resistivity depends on temperature [23-25]. Once the surface temperature of the film is known from the calibrated resistance versus temperature relationship, an inverse technique is utilized to deduce the heat flux data corresponding to the temporal evolution of the measured surface temperature [26-28]. However, the thin film gauge itself, cannot isolate radiative flux from other heat transfer mechanisms. Long enough distance between the plasma
source and the gauge or placement of transparent windows over the gauge can ensure measurement of radiative flux alone, preventing other modes of heat transfer. Issues related to design optimization of fast-response gauges have been discussed [29].

Figure 2.3 shows the basic design of the thin film heat flux gauge. The polyimide layer, which is 50 µm thick has a low thermal conductivity (0.1 to 0.35 W/m K) and is chemically stable for working temperatures up to 250 to 320°C [30]. Sputtering of platinum at 0.67 Pa was employed to yield films that attach well to the polyimide substrate. The thickness of the sputtered platinum is typically 80 nm, and its width and length are, respectively, 0.25 and 12 mm. At each end of the platinum strip, 3 mm wide copper leads of 500 nm thickness and 6 mm length were sputtered on top of the platinum. The electrical leads are soldered onto the copper lead, to yield a high-strength and high-electrical conductivity connection. A transfer tape is used to attach the polyimide film to the SS304 substrate. The constant current source is National Semiconductor’s LM 134 chip, powered by a low-noise 9V battery. The external resistor $R_{\text{set}}$ defines the current flowing through the gauge. The current is nominally set at 3 mA. This value produces insignificant self heating of the gauge, while providing adequate protection to electrical noise produced early in the discharge process. Figure 2.4 shows the response of the electrical circuit to a step increase in the resistance; that is, the switch is suddenly opened. It is clear that the internal circuitry of the LM 134 constant current source responds quickly to the sudden change in resistance. Since the platinum film is thin and located on a poorly conducting substrate, the frequency response is high (>100 kHz), and it is controlled by the electrical circuit of the constant current source.
Figure 2.3. Electrical circuit and layer design for platinum heat flux gauge.

Figure 2.4. Response of circuit containing LM 134 constant current source to a step increase in the resistance.
2.3.3 Data Reduction

A standard inverse approach was employed to estimate the transient, absorbed radiative heat flux variation from the measured time-dependent voltage data. The model assumes that conductive transfer in the polyimide film is one-dimensional, that a perfect thermal contact is made between the platinum film and the polyimide substrate, and that thermophysical properties are constant. The inverse problem is governed by

\[ k \frac{\partial^2 T}{\partial x^2} = \rho c \frac{\partial T}{\partial t} \quad \text{for} \quad 0 < x < \infty, \quad 0 < t < t_f \]  

\[ -k \frac{\partial T}{\partial x} = q^*(t) \quad \text{at} \quad x = 0 \]  

\[ T = T_{ref} \quad \text{at} \quad x \to \infty \]  

\[ T = T_{ref} \quad \text{at} \quad t = 0 \]

where \( q^*(t) \) is the unknown, absorbed radiative heat flux. Based on the conjugate-gradient approach described in detail by Ozisik [28], a numerical procedure was developed. The inverse data reduction technique was applied to the measured surface temperature to determine the absorbed, radiative heat flux. The model used a thermal conductivity \( k = 0.25 \text{ W/m K} \), which is the normal conductivity obtained by Kurabayashi et al. [31], \( \rho = 1,420 \text{ kg/m}^3 \), and \( c_p = 1,040 \text{ J/kg K} \) of the polyimide substrate.

Since the width of the platinum is 250 µm and that the polyimide thickness is 50 µm, the use of a one-dimensional film may raise concerns. It is possible to estimate the thermal wave penetration based on a uniform heat flux during a specified time interval. The analysis results in a thermal wave penetration depth \( \delta \approx 2(\alpha \times t)^{1/2} \). With a
maximum duration of about 300 µs of the plasma emission, the thermal wave penetration depth is approximately 14 µm. Hence, the use of a one-dimensional heat conduction model is very reasonable.

The temperature coefficient of the electrical resistivity of platinum $\beta = 0.002/K$ was assumed to be linear over the temperature range from 20°C to 220°C, and it was deduced from measurements using a standard convection oven. This value is about 50% lower than the bulk value (0.00389/K). For the manufactured film thickness of 80 nm, the incident radiant energy is either absorbed or reflected by the platinum film; the transmissivity is practically zero. The theoretical spectral absorptivity of platinum can be roughly estimated using bulk properties [32]. The diffuse or normal spectral absorptivity is about 0.75 at 200 nm, decreases to 0.4 at 400 nm, and about 0.32 at 600 nm. The platinum film appears slightly dark to the naked eye.

### 2.4 Discussion of Results

Figures 2.5 and 2.6 show eight images acquired by the Cordin 222-B CCD camera using an exposure time of 70 ns, with the first (top) image 40 µs after triggering and subsequent images separated by 20 µs. Images after 100 µs reveal a rapid decay of the plasma emission, with the 8th image showing only weak structures remaining of the plasma. The fourth image at $t = 100$ µs reveals that the gauge at the stagnation point ($P_0/T_0$) is covered by the plasma for all hemispherical solid angles. Plasma expansion, however, is significant resulting in partial coverage for the outermost gauge position.
(P4/T4), which is located 38 mm from the stagnation point. Clearly, plasma emission is most significant in the region to the right of the Mach disc, which shows some curvature. General features of the under-expanded jet have been discussed elsewhere [5, 7-8, 33].

Figure 2.5. Side-view images of plasma obtained from a charging level of 2.5 kV, and acquired 40 (top), 60, 80 and 100 µs (bottom) after triggering.
Figure 2.6. Side-view images of plasma obtained from a charging level of 2.5 kV, and acquired 120 (top), 140, 160 and 180 µs (bottom) after triggering.
Figures 2.7, through 2.9 show the results from open-air testing involving a distance between plasma exit port to stagnation plate of 50 and 75 mm, as well as charging voltages of 2.5, 3.0 and 4.0 kV. Figure 2.7 reveals that, irrespective of charging voltage, peak values of current i1 are reached at about 80 $\mu$s into the event. However, the duration of electrical energy conversion varies from about 190 to 220 $\mu$s. Current i1 represents the current flow through the plasma chamber. At the end of the i1 current flow, there is still some residual energy in the capacitor, however. It is slowly dissipated in the noninductive bypass resistor, which is used to deduce the instantaneous voltage drop across the plasma. The output from Diode 1, shown in Fig. 2.8, reveals that the larger the charging voltage, the earlier the plasma emerges into the ambient air. This earlier plasma emergence is caused by increased rate of electrical energy conversion, producing a more rapid increase in pressures within the capillary and thus an earlier emergence of the plasma. For example, a charging voltage of 4.0 kV, plasma emergence occurred 25 $\mu$s after triggering, whereas the corresponding time was 32 $\mu$s for a charging level of 2.5 kV. Hence, times prior to plasma emergence are of little interest for both gas dynamic and heat transfer studies. The response of the second diode, shown in Fig. 2.9, does show the plasma emergence too at this early time, but this is caused by multiple reflections within the test facility. Diode 1, however, records peak radiant heat fluxes that are much larger than Diode 2. The occurrence of the peak value of the heat flux of Diode 1 is close to the occurrence of the peak value of the current i1. Diode 2 detects reemission in some tests after the completion of the electrical discharge ($t > 220 \mu$s), which is probably due to interactions between plasma species and air, as well as
recombination reactions among the plasma products. For small charging levels, the emission from the plasma is quite small. Diode 2 senses emission only from regions near the stagnation plate; since it very low compared to Diode 1, the plasma has cooled significantly once reaching the stagnation plate.

Figure 2.7. Current and voltage drop in electrical circuit for a 3.2 mm diameter polyethylene capillary for charging voltages of 2.5 kV (0.6 kJ), 3.0 kV (0.86 kJ), and 4.0 kV (1.56 kJ).
Figure 2.8. Response of Diode 1 due to emission from ablated products from polyethylene capillary, initiation wire and nozzle for charging voltages of 2.5 kV (0.6 kJ), 3.0 kV (0.86 kJ), and 4.0 kV (1.56 kJ).

Figure 2.9. Response of Diode 2 due to emission from ablated products from polyethylene capillary, initiation wire and nozzle for charging voltages of 2.5 kV (0.6 kJ), 3.0 kV (0.86 kJ), and 4.0 kV (1.56 kJ).
The heat flux gauges were covered with two fused silica windows (one is 1.59 mm thick, whereas the other is 4.76 mm thick); this window material is very pure and allows transmission over the wavelength range from about 170 nm to 2,500 nm. The thin, sacrificial window is replaced after every test, since some slight degradation occurs of the surface. Additionally, only a small amount of sooty residue remains on the surface, in particular for the low charging level of 2.5 kV. The LM134 constant current source is susceptible to interference from the rapidly changing electric and magnetic fields during the first 20 µs after triggering. Using a capacitor across the battery terminals has no effect. This interference is caused by two effects that produce high frequency electric and magnetic fields. First, as the initiation wire is rapidly heated to its melting point, its electrical conductivity rapidly decreases as the wire expands due to thermal effects and breaks apart to form small droplets. Second, as arcing occurs between the droplets, a highly conductive plasma is rapidly produced. During the plasma transitions from one containing metal ions and atoms to another containing carbon and hydrogen ions and atoms, as well as hydrocarbon ions and molecules, the electrical conductivity changes again. Once the plasma emerges from the capillary, a quasi-steady voltage is achieved until the electrical energy is nearly discharged.

Figures 2.10 through 2.13 show the pressure, gauge temperatures, and deduced absorbed radiant heat fluxes for charging levels of 2.5 and 3.0 kV and distances between plasma chamber and stagnation plate of 50 and 75 mm; \( T_{\text{ref}} = 20^\circ \text{C} \). The case shown in Fig. 2.10 yields the peak values: the film temperature rise is 160°C, the peak pressure is 8.8 bar, and the peak heat flux is 14.4 MW/m². Increasing the distance between plasma chamber and stagnation by 25 mm has a pronounced effect, as shown in Fig. 2.11. The
peak film temperature is only $56^\circ C$ and heat flux reaches a peak of only about 3.8 MW/m$^2$. Increasing the charging level from 2.5kV to 3kV, shown in Fig. 2.12, yields a doubling in the peak heat flux, whereas the electrical energy stored in the capacitor is increased only by 44%. Examining the results for a gauge location of 9.5 mm above the stagnation point, shown in Fig. 2.13, reveals a 20% reduction in the peak heat flux. Hence the view factor between the plasma and gauge location is important, suggesting the need for multi-dimensional radiation models if this problem is to be studied using computational techniques. The gas dynamic phenomena revealed by the pressure gauges are complex as discussed previously, and their general features are captured in the comprehensive modeling efforts by Nusca et al. [33].

![Figure 2.10. Pressure, temperature and heat flux at the stagnation location for a charging voltage of 2.5 kV (0.6 kJ) and a distance of $L = 50$ mm between plasma port and stagnation plate.](image-url)
Figure 2.11. Pressure, temperature and heat flux at the stagnation location for a charging voltage of 2.5 kV (0.6 kJ) and a distance of $L = 75$ mm between plasma port and stagnation plate.

Figure 2.12. Pressure, temperature and heat flux at the stagnation location for a charging voltage of 3.0 kV (0.86 kJ) and a distance of $L = 75$ mm between plasma port and stagnation plate.
Figure 2.13. Pressure, temperature and heat flux at a distance 9.5 mm above the stagnation location (gauge 1) for a charging voltage of 2.5 kV (0.6 kJ) and a distance of \( L = 50 \text{ mm} \) between plasma port and stagnation plate.

The temperature rise of the heat flux gauges is dominated by plasma emission during the time period prior to arrival of the precursor shock and shows a fairly smooth variation. After the peak of the electrical energy conversion, the plasma quickly loses its sensible energy largely by radiation, and thus the gauge temperature decreases quickly due to primarily heat conduction into the substrate and secondarily to surface emission. Furthermore, inspection of Figs. 2.10 through 2.13 reveals that the early portion of the plasma emission is the most intense, corresponding to the time period up to peak current flow, or peak power dissipation within the capillary. From other measurements, the plasma has traveled only about 40 mm at a time of 80 \( \mu s \) into the event.

Increasing the distance from 50 to 75 mm has a pronounced effect on all the peak values, demonstrating the important effect of gas dynamic expansion, directional nature of radiation, heat loss by radiation, and possibly recombination reactions among plasma
species. A two-stage radiant heating effect is observed clearly in Figs. 2.10 and 2.13, whereas it is only slightly detected in Fig. 2.11. The first stage is caused by the strong plasma emission prior to arrival of the precursor shock. The second stage is likely caused by increased pressure and temperature near the stagnation point, as plasma accumulates and recombination reactions occur, some of which may produce emission due to electronic transitions in atomic and molecular species. Figures 2.10 and 2.13 show that small but measurable differences in pressure arrival and magnitude, as well as temperature and deduced radiant heat flux, occur between gauges located at the stagnation point and 9.5 mm above the stagnation point. The gas dynamic phenomena also show a slight phase shift in Figs. 2.10 and 2.13.

The plasma radiation is both spectral and directional, and has a strong nonlinear dependence on temperature. To push the gauges to their limits and beyond, we show in Figs. 2.14 and 2.15 the results for a charging level of 4kV and distance of 50 mm. Of the five gauges used on the stagnation plate, three were completely vaporized, a fourth was damaged, whereas the outermost gauge survived. Since the calibration was performed up to a temperature of 220°C, the results for gauges 0 and 2 are terminated near 280°C. The observed phenomena discussed previously are evident again, largely by gauge 4 which is located 38 mm above the stagnation point. The peak level of the radiative heat flux of gauge 4 is slightly above 20 MW/m², whereas much higher values would be reached at the stagnation point. Plasma emission is dominant prior to arrival of precursor shock, during which some of the oscillating gas dynamic effects can be seen in the deduced radiative heat flux; plasma emission is much lower after the electrical discharge is complete.
Figure 2.14. Temperature of three heat flux gauges separated by 19 mm on the stagnation plate for a charging voltage of 4.0 kV (1.56 kJ), and a distance of \( L = 50 \) between plasma port and stagnation plate.

Figure 2.15. Deduced absorbed radiative heat flux of three gauges separated by 19 mm on the stagnation plate for a charging voltage of 4.0 kV (1.56 kJ), and a distance of \( L = 50 \) between plasma port and stagnation plate.
In order to assess the role of the fused silica window and its effect on the deduced radiative heat flux, Fig. 16 shows the results with and without the fused silica window for gauges mounted 75 mm below the plasma port. These results were obtained from averaging data from three experiments and four heat flux gauges; the effect of gauge position is not significant when mounting gauges below the plasma. Inspection of the results in Fig. 16 reveals that a reduction of only about 12% is obtained by using the fused silica window. This reduction is quite acceptable, since the spectral transmissivity of the window ranges from about 0.92 at 200 nm to 0.94 at 700 nm (data from ESCO Products). Hence, the effect of the direction of the radiant energy emitted by the plasma on the deduced absorbed radiant flux levels in the previous figures is at best marginal. Furthermore, these results also suggest that the spectral range from about 200 nm to 2,500 nm of the fused silica window includes the dominant fraction of the radiant energy emitted by the plasma. Rovibrational transitions in the infrared wavelength range beyond 2,500 nm by molecular species, such C$_x$H$_y$, do not appear to contribute significantly to the radiative heat flux, although Diode 2 did record some effects from electronic transitions in the visible wavelength range well beyond the conclusion of the electrical power conversion as mentioned previously. Additionally, the error bars included represent a 99% confidence interval, which is obtained by multiplying the standard deviation by 2.565 and dividing by the square root of the degrees of freedom.
Figure 2.16. Deduced radiative heat flux for gauges located below the plasma with and without fused silica window.

It is well known that inverse techniques are susceptible to error magnification. That is, a relatively small uncertainty in an input parameter may cause a large uncertainty in the estimated values. In the present combined experimental and numerical effort, the thermal conductivity of polyimide and the temperature coefficient contains the largest uncertainty. Other input values are the density and specific heat, but the uncertainties of these values are usually much smaller. Figure 17 shows the effects of varying the input parameter on the estimated radiative heat flux. It observed that over the range of change in thermophysical properties, the response is reasonably linear. Within the algorithm, the temperature coefficient $\beta$ and the term $\alpha^{0.5}k^{-1}$ appear as a product, thus showing the identical results in Fig. 17. The uncertainty in the measured temperature coefficient is
approximately 10%, suggesting a similar uncertainty in the estimated radiant heat flux. However, experiments will be conducted in the future to determine the thermal conductivity of the polyimide film, which may be anisotropic.

![Figure 2.17. Effect of uncertainty in electrical and thermal transport input data on the deduced radiative heat flux.](image)

To demonstrate the temporal effect of uncertainty in the thermal conductivity and the temperature coefficient of the electrical resistivity, Figs. 18 and 19 show the results of the estimated radiative heat flux at the stagnation point for a distance of 50 mm between plasma port and stagnation plate, and a charging level of 2.5kV. These two input parameters were changed in increments with a maximum of ± 20% in the inverse
technique. Inspection of these results show that the trends remain the same, and that peak values do not shift temporally. That is, a large uncertainty early in the event does not affect the results later in the event.

Figure 2.18. Effect of uncertainty in thermal conductivity on the deduced radiative heat flux.
Figure 2.19. Effect of uncertainty in the temperature coefficient of the electrical resistivity on the deduced radiative heat flux.

Apart from the thermophysical properties, several other sources can contribute to measurement uncertainties. One of these is the possible atmospheric attenuation, especially for wavelengths lower than 300 nm. Another possible source of uncertainty is the vapor shield created by plasma condensation on the window, preventing radiative flux to reach the gauge. [16, 34-37] In the present configuration, however, the radiative flux attains its peak before the plasma reaches the window, confining the possible vapor shield effect to the later part of the event only. The potential presence of a vapor shield requires further investigation. Experiments, however, were conducted to identify the effect of
material deposition over the sacrificial windows. Two consecutive experiments without replacing the sacrificial window showed a 7% maximum deviation in measured heat flux.

2.5 Conclusions

The use of thin platinum films sputtered on a polyimide substrate has been described for deducing the transient variation of the absorbed radiative heat flux emitted from a plasma produced by a capillary discharge. The major findings from this study are as follows.

1. The radiative heat flux reached a maximum when the electrical power conversion reached a maximum.

2. The spectral transmission range of the fused silica window indicates that the major fraction of the radiative heat transfer occurred from about 170 to 2,500 nm.

3. Once arrived at the location of the heat flux sensors, the emission from the plasma is significantly reduced compared to its peak values, as a result of significant radial expansion of the plasma and rapid heat losses by radiation in all directions.

Present study deals with radiative heat transfer from plasma produced by relatively low charging voltages. Future studies will consider other geometries, higher charging voltages, different capillary, wire and window materials, as well as other heat transfer mechanisms.
2.6 References


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Chapter 3

MATERIAL DEPENDENCE OF ETC PLASMA RADIATION

3.1 Abstract

Previous chapter described the thermofluid dynamics of electrothermal-chemical plasma jet, as well as preliminary measurements of transient radiant heat flux, stagnation pressure, and electrical parameters. This focus of the present chapter is to identify the effect of capillary and trigger wire materials on the radiative heat transfer from the capillary-sustained plasma jet. The results show that appreciable differences are present among the capillary and wire combinations, with a polycarbonate capillary and copper wire yielding the largest energy deposition in the substrate, whereas Teflon-nickel the lowest.

3.2 Introduction

Electrothermal-chemical (ETC) ignition of solid propellants, showing several advantages over the conventional chemical ignition, has recently received considerable attention [1-9]. In a typical ETC ignition system high-temperature, high-pressure plasma jet directly impinges on the propellant surface. Radiative heat transfer is generally regarded as an important mode of energy transport during plasma-propellant interaction [10-13]. It is, however, observed that, use of long capillary, and thick trigger wire, increases capillary ablation but reduces radiative effects [14-18].
Early attempts of transient radiant heat flux measurement by Ryan et al. [19], using commercial heat flux gages, captured substantial electrical noise, but indicated high radiative flux level. Infrared imaging technique by Williams and White [20] was particularly successful in deducing the average radiant heat flux. Further studies also identified the dependence of average radiant flux on plasma pulse length [21-22]. Numerical studies of Gruber et al. [23], and Kappen and Bauder [24-25] revealed that UV radiation dominates over IR during plasma propellant interaction.

The above discussion reveals a variety of approaches are utilized to ascertain the radiative characteristics of capillary sustained plasma, which may account for improved ignition of solid propellants. Present research aims to contribute to the understanding of the capillary and wire material dependence of transient radiative heat flux from an ETC plasma jet. Following a similar procedure of Das et al. [10], described in the previous chapter, nine different combinations of capillary-wire materials have been investigated. Transient pressure, temperature and radiant heat flux measurements have been carried out, along with flow visualization.

### 3.3 Experimental Apparatus and Approach

Previous chapter presented detail description of the experimental apparatus, approach, and data reduction procedure. Data reduction technique uses one-dimensional inverse approach described in detail by Ozisik [26]. Thermal conductivity of polyimide substrate ($k = 0.25$ W/m K) was acquired from recently published results [27]. Using bulk radiative properties of platinum [28-29], the diffuse or normal spectral absorptivity of the
thin film platinum gage is found to be about 0.75 at 200 nm, decreases to 0.4 at 400 nm, and about 0.32 at 600 nm.

### 3.3.1 Capillary and Wire Materials

Three different materials are used for the capillaries: high-density polyethylene (PE), polycarbonate (popularly known as Lexan, LE) and polytetrafluoroethylene (Teflon®, TE). These materials were acquired from McMaster-Carr and machined to appropriate dimensions using standard techniques. The molecular structures of monomer units of these compounds are shown in Fig. 3.1. The effects of three different wire materials were examined: copper (Cu), nickel (Ni) and aluminum (Al). For all the experiments, trigger wire mass is kept 3.6mg. The high pressures and temperatures within the capillary are generally believed to completely vaporize the initiator wire. However, the extent of ablation of the capillary is strongly dependent on its physicochemical properties shown in Table 3.1. There are numerous studies available in the literature that have attempted to elucidate the thermal decomposition characteristics of these capillary materials under low heating rates, with and without the use of catalyst.
Figure 3.1. Molecular structures of repeated monomer units in (a) bisphenol A polycarbonate (Lexan), (b) polyethylene, and (c) polytetrafluoroethylene (Teflon®).

Table 3.1. Relevant physicochemical properties of capillary and wire materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$c$ (kJ/kg K)</th>
<th>$k$ (W/m K)</th>
<th>$T_{melt}$ (K)</th>
<th>$T_{dec}$ (K)</th>
<th>$T_{boil}$ (K)</th>
<th>$h_{fg}$ (kJ/kg)</th>
<th>$I_{pot}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>950</td>
<td>1900</td>
<td>0.49</td>
<td>390</td>
<td>670-800</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>LE</td>
<td>1200</td>
<td>1200</td>
<td>0.20</td>
<td>–</td>
<td>670-800</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>TE</td>
<td>2200</td>
<td>1000</td>
<td>0.25</td>
<td>617</td>
<td>770-920</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Al</td>
<td>2700</td>
<td>900</td>
<td>237</td>
<td>933</td>
<td>–</td>
<td>2740</td>
<td>10800</td>
<td>5.99</td>
</tr>
<tr>
<td>Cu</td>
<td>8960</td>
<td>385</td>
<td>401</td>
<td>1356</td>
<td>–</td>
<td>2840</td>
<td>4796</td>
<td>7.73</td>
</tr>
<tr>
<td>Ni</td>
<td>8900</td>
<td>444</td>
<td>91</td>
<td>1726</td>
<td>–</td>
<td>3005</td>
<td>6378</td>
<td>7.63</td>
</tr>
<tr>
<td>H</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>13.59</td>
</tr>
<tr>
<td>C</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>11.26</td>
</tr>
<tr>
<td>N</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>14.53</td>
</tr>
<tr>
<td>O</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>13.61</td>
</tr>
<tr>
<td>F</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>17.40</td>
</tr>
</tbody>
</table>
The thermal stability of Teflon is largely derived from the strong C-F bond of 507 kJ/mol, compared to typical values of 415 kJ/mol for C-H and 348 kJ/mol for C-C bonds [30, 31]. Using thermogravimetric techniques with heating rates at 25 K/min, melting of Teflon is observed around 617 K, noticeable decomposition begins to occur around 770 K, and complete decomposition is observed near 920 K in atmospheric conditions. Decomposition products include \( \text{C}_2\text{F}_4 \), \( \text{C}_3\text{F}_6 \) and \( \text{C}_4\text{F}_8 \) [32]. Ceramics, such as Si and \( \text{CaSi}_2 \), produce exothermic decomposition whereas Fe and \( \text{FeSi} \) yield endothermic decomposition. Fe has nearly no effect on the kinetic rates of decomposition. Additionally, it should be noted that Teflon can be used as an oxidizing agent, although the strong C-F bond [33]. Flares and igniters often utilize a metal/PTFE/Viton combination to produce combustion products of very high temperatures [34]. PTFE is also considered for use in pulsed plasma thrusters [35].

Polyethylene is a rather soft material compared to Teflon. As a result, the high pressures within the PE capillary are likely to cause a volumetric expansion. Thermogravimetric techniques, with a heating rate of 25 K/min, reveal melting near 388 K, onset of decomposition around 670K, and complete decomposition near 800 K [36]. The gaseous products contain a large fraction of C3 compounds, whereas the residue is comprised of largely aromatics [37-38].

Polycarbonates are commonly used in rewritable compact discs, eye glasses, medical parts, aircraft and appliances due to its toughness, transparency, good mechanical and thermal stability. Using thermogravimetric techniques at 10 K/min, onset of decomposition occurs around 670 K and is complete near 800 K [39]. Gaseous products
evolved at temperatures from 770 to 820K contain a wide variety of compounds, suggesting many different pyrolysis processes [40].

The PE and LE compounds have also been subjected to high heating rates and temperatures due to an arc jet environment [41]. Temperatures of 5,100 K were lower than those deduced from capillary discharges of 10,000 to 50,000 K [42, 43]. As such, radiative contributions from ions, ion recombination reactions, and atomic species are likely to be larger contributors to radiative heat transfer from capillary discharges compared to the arc jet environment. Using spectrographic techniques covering a wavelength range from 250 to 870 nm, species identified in the arc jet as having significant contributions include the C2 swan band, CN red and violet bands, CO Asundi band [44], and CH, as well as chemiluminescence from CO+O [41]. Hence, reactions between pyrolysis products from the ablated plastics and ambient air will produce species that contribute significantly to the radiative heat transfer in capillary discharges as well.

3.4 Discussion of Results

The use of the basic RLC-electrical circuit yields highly repeatable data from the two current transducers, pressure transducers, and heat flux gauges. Deviations in these measured parameters are typically only a few per cent between the experiments, resulting in a small uncertainty. A larger uncertainty is obtained for the deduced radiative heat flux, which is inherent in the use of inverse techniques. The uncertainties are indicated by error bars at ±2σ, where σ is the standard deviation based on three independent
estimations. Electrical noise is most pronounced during the first 20 \( \mu s \), or when the plasma is being formed. Some additional noise occurs during voltage reversals, which occur because the electrical circuit is slightly under-damped. A charging voltage of 2.5 kV, trigger wire mass of 3.6 mg, and distance between capillary exit nozzle and stagnation plate of 50 mm were kept constant; all experiments were conducted in an open-air environment. The discussion of results is first focused on differences in the voltage and current traces for the various capillary and wire combinations.

Figure 3.2 shows the acquired voltage and current in the capillary. The corresponding data, for ablated mass from the various components are shown, in Table 3.2. Here, the elkonite nozzle, which is a tube of 25 mm in length and 3.2 mm in diameter, is also the negative electrode. Several interesting features are observed. First, the trigger wire has the largest influence on the variation on the voltage drop across electrodes attached to the capillary and the current flow within the capillary. The Al wire, with its relatively low melting and boiling points as well as a low ionization potential, provides the smoothest transition from current flow in the wire to current flow within the plasma. Since the current flow varies smoothly throughout the event and the charging energy level is kept constant, peak values are slightly lower than those obtained from using either the Cu or Ni wires. The Ni produces the largest delay in current flow, from about 10 to 20 \( \mu s \), probably due in large part its higher melting and boiling points, and about its twice molecular weight compared to Al. That is, fewer Ni atoms are available to become charge carrier compared to Al. Another important property is surface tension of the molten trigger metal, which forms small droplets during the transition to a gaseous
state within the capillary to form a plasma. The initiation transients of plasma formation have been discussed elsewhere [16, 45-47].

Figure 3.2. Voltage and current within capillary during discharge of 0.6kJ of electrical energy (2.5kV) for different capillary and initiator wire materials.
Second, the use of the TE capillary yields the highest values of the peak currents and thus generally the lowest average voltages. This may suggest that the total number of charge carries within the plasma is the largest for TE capillary. Such a finding would be quite surprising, since TE is the most thermally stable material of the three capillaries. From the results shown in Table 3.2, approximately 0.68 mmoles of TE is ablated (considering only the monomer structure of Fig. 2), whereas 0.89 and 1.41 mmoles are ablated from the LE and PE capillaries, respectively. Hence, a mechanism of extensive carbon and fluorine ionization can possibly explain the efficient charge transport through TE capillary.

Table 3.2. Mass ablated as well as average voltage and current for different capillary and wire material combinations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ablated mass (mg)</th>
<th>Capillary (%)</th>
<th>Nozzle (%)</th>
<th>Electrode (%)</th>
<th>Wire (%)</th>
<th>$V_{ave}$ (kV)</th>
<th>$I_{ave}$ (kA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE+Cu</td>
<td>6.93</td>
<td>26.44</td>
<td>15.53</td>
<td>6.10</td>
<td>51.93</td>
<td>1.007</td>
<td>2.609</td>
</tr>
<tr>
<td>PE+Al</td>
<td>6.57</td>
<td>17.26</td>
<td>20.66</td>
<td>7.25</td>
<td>54.13</td>
<td>0.984</td>
<td>2.649</td>
</tr>
<tr>
<td>PE+Ni</td>
<td>6.19</td>
<td>26.39</td>
<td>11.68</td>
<td>3.76</td>
<td>58.17</td>
<td>1.070</td>
<td>2.632</td>
</tr>
<tr>
<td>LE+Cu</td>
<td>6.95</td>
<td>40.26</td>
<td>5.42</td>
<td>2.55</td>
<td>51.77</td>
<td>1.000</td>
<td>2.719</td>
</tr>
<tr>
<td>LE+Al</td>
<td>7.15</td>
<td>32.60</td>
<td>8.43</td>
<td>9.03</td>
<td>50.33</td>
<td>0.961</td>
<td>2.715</td>
</tr>
<tr>
<td>LE+Ni</td>
<td>6.52</td>
<td>38.34</td>
<td>2.04</td>
<td>4.41</td>
<td>55.21</td>
<td>1.076</td>
<td>2.832</td>
</tr>
<tr>
<td>TE+Cu</td>
<td>10.83</td>
<td>56.31</td>
<td>7.89</td>
<td>2.57</td>
<td>33.23</td>
<td>0.990</td>
<td>2.922</td>
</tr>
<tr>
<td>TE+Al</td>
<td>10.20</td>
<td>54.24</td>
<td>6.44</td>
<td>4.03</td>
<td>35.29</td>
<td>0.970</td>
<td>2.778</td>
</tr>
<tr>
<td>TE+Ni</td>
<td>11.23</td>
<td>57.86</td>
<td>8.31</td>
<td>1.78</td>
<td>32.05</td>
<td>1.054</td>
<td>2.949</td>
</tr>
</tbody>
</table>
Third, it is difficult to ascertain when the plasma transitions from one largely containing atoms and ions from the trigger wire to another containing largely atoms and ions from the trigger wire and ablated capillary. Since the decomposition temperatures of the capillary materials do not vary significantly and that pressures and temperatures rapidly increase to extremely high levels, the plasma is believed to contain species from the capillary very early in the event. For the case involving TE, this is most likely in the time interval from 20 to 30 µs into the event.

Figure 3.3 shows the transient temperature, radiant heat flux and stagnation pressure variation on the stagnation plate at the exit port centerline for the PE capillary and Cu, Al, and Ni trigger wires. Also here, several distinct differences are observed. The use of the Al wire, with its smoothly varying current, produces the largest peak radiant heat flux. The radiant heating begins around 40 µs into the event, indicating that plasma emergence is rapid. Peak radiant heat fluxes are obtained prior to arrival of the precursor shock, and they generally coincide with the peak of the current flow. Cases with Cu and Ni wires suggest a slight change or increase (second rise) when peak stagnation pressures are achieved. It is not clear if this effect is a chemically induced effect caused by reactions between Ni and surrounding air, or differences in the radiative properties between Al, Cu and Ni. The secondary increased radiative heat flux for Cu and Ni is not caused by the arrival of particles (from wire or nozzle), since the quartz window remains quite clear after one firing. However, inspection of atomic line data reveals that neutral and singly ionized Al has relatively few lines produced by electronic transitions covering wavelengths from 200 nm to approximately 700 nm, whereas Cu and Ni have a much larger number of lines [48]. Any further assessment regarding spectral emission
Figure 3.3. Transient variation of pressure, temperature and heat flux at the stagnation location for polyethylene capillary and different wire materials with a charging voltage of 2.5 kV and a distance of 50 mm from plasma exit port to stagnation plate.
characteristics requires additional experiments. The compressible flow produces strong pressure oscillations that appear quite insensitive to the type of trigger wire material used. The large peak radiant heat flux from the case with Al wire may only partially contribute to a reduced plasma temperature and thus produces the lowest peak pressure; the reduction is much more likely due to a lower plasma density. The differences in peak temperatures between the three wires remain quite small or about 7 K, suggesting that differences in the integrated absorbed heat flux (amount of energy absorbed) are also quite small.

Figures 3.4 and 3.5 show, respectively the radiative heat flux, temperature and stagnation pressure for LE and TE capillaries, respectively. The trends observed in Fig. 3.3 remain, although the magnitudes are considerably different. First, the LE-Cu combination produces peak temperatures of nearly 200°C of the heat flux gauge, compared to the lowest of about 150°C for the PE-Ni combination; hence the absorbed energy flux is significantly higher for the LE-Cu combination, which then most likely would produce the highest probability of transition from ignition to combustion of an energetic material. The PE capillary produces generally the lowest temperatures. The use of the Ni trigger wire yields consistently the lowest radiative heat fluxes. However, the TE capillary consistently yields the largest stagnation pressure, although the fewest number of moles are ablated. To shed some light on these findings, it is instructive to examine CCD images for selected capillary trigger wire combinations.
Figure 3.4. Transient variation of pressure, temperature and heat flux at the stagnation location for Lexan capillary and nickel wire with a charging voltage of 2.5 kV and a distance of 50 mm from plasma exit port to stagnation plate.
Figure 3.5. Transient variation of pressure, temperature and heat flux at the stagnation location for Teflon capillary and different wire materials with a charging voltage of 2.5 kV and a distance of 50 mm from plasma exit port to stagnation plate.
Figure 3.6 shows images acquired by the Cordin 222-B CCD camera with the first (top) image 80 µs after triggering and subsequent images separated by 10 µs. Thus the time interval of the primary and secondary rises in the heat flux is covered. Images were captured for three different capillary-wire material combinations: PE-Cu, LE-Al, and TE-Ni. Exposure time (20 ns) and aperture (f/11) were kept constant for all the images authorizing image brightness to be an indication of the plasma temperature [42]. The middle image corresponds to peak pressure and possible arrival of precursor shock, which should be close to jet surface at this time. The images reveal possible highest temperature plasma generation for the LE-Al case, followed by PE-Cu and TE-Ni, respectively. Again a smaller radial expansion of the jet along with a higher mass ablation that produces a larger density, may eventually explain higher stagnation pressure of TE capillaries. The lower-density plasma from PE in general produces the lower stagnation pressures. The LE-Al combination produces the largest radial expansion due to very high plasma temperatures and pressures. In addition, the primary and secondary peaks in the emitted radiant flux are observed in the images of Figs. 3.6a and c, whereas Fig. 3.6b for Al shows a gradual decrease in brightness from top to bottom pictures. General features of the under-expanded supersonic jets have been discussed elsewhere [6, 8, 9, 49].
Figure 3.6. Side view images of plasma for a charging voltage of 2.5 kV, acquired at 80 (top), 90, 100, 110, 120 µs (bottom) after triggering, for (a) polyethylene capillary and Cu wire, (b) Lexan capillary and Al wire, and (c) Teflon capillary and Ni wire.
To provide information on the profile of the radiative heat flux and temperature, values at four additional gauge locations are provided in Figs. 3.7 and 3.8, respectively. The distance between each gauge is 9.53 mm. A total of five gauges are used. Examination of Figs. 3.7 and 3.8 reveals that the radiative heat flux decays considerably away from the centerline of the jet for any capillary and wire material combination. The outer-most gauge is located 38 mm from the centerline. Comparison with Fig. 3.7 shows that this gauge is close to the edge of the Mach disc. It is also interesting that the PE-Ni plasma shows the least radial decay, the basis for which is not fully clear. Ni trigger wire clearly plays an important role, as the other LE-Ni and TE-Ni, also show the lowest radial decay.

Figure 3.7. Variation of peak heat flux with radial distance from centerline for a 2.5 kV (0.6 kJ) capillary plasma and a distance of 50 mm between plasma port and stagnation plate.
Figure 3.8. Variation of peak temperature with radial distance from centerline for a 2.5 kV (0.6 kJ) capillary plasma and a distance of 50 mm between plasma port and stagnation plate.

Temperature rise of a heat flux gauge indicates absorption of radiant energy at the gauge location. The present studies, however, display several cases of multi-stage temperature rise along with material dependence of spatial and temporal temperature gradient. The absorbed radiant energy at a location can, therefore, be determined only by numerically integrating the discrete heat flux data over time. Fig. 3.9 presents the radial variation of absorbed radiant energy per unit area. The radiative heat fluxes are integrated over 25 to 500 µs, as the transient flux levels are significant in this period. Closely following the pattern of Fig. 3.8, the results expectedly places LE-Cu combination at the top, followed by TE-Cu.
Figure 3.9. Variation of absorbed radiant energy per unit area with radial distance from centerline for a 2.5 kV (0.6 kJ) capillary plasma and a distance of 50 mm between plasma port and stagnation plate.

3.5 Conclusions

Capillary and trigger wire material dependence of the radiative heat flux from an electrothermal chemical plasma jet were investigated experimentally. Thin platinum film sputtered on a polyimide substrate was utilized for deducing the transient variation of the absorbed radiative heat flux emitted from the plasma produced by the capillary discharge. Three different capillary materials (polyethylene, Lexan and Teflon) along with three different initiation wire materials (copper, aluminum and nickel) were studied. All the experiments were conducted in an open-air atmosphere with a constant charging voltage (2.5 kV) and wire mass (3.6 mg). The major findings from this study are as follows:
1. The Lexan capillary with Al trigger wire generates the largest peak radiative heat flux, owing in large part to the low melting and boiling temperatures as well as ionization potential of aluminum.

2. The Lexan capillary with Cu wire produce a substantially higher absorbed energy flux compared to the other capillary and wire combinations.

3. Depending on the capillary and wire material combinations, radiative heating can be single- or multi-staged; the latter possibly involves exothermic recombination reactions.

4. Peak heat flux and temperature decay significantly at positions away from the centerline, with the maximum always occurring at the centerline of the plasma jet.

5. The use of Teflon capillary yields the largest stagnation pressures possibly due to a large density of the plasma.

The present study deals with the radiative heat transfer from plasma produced by relatively low charging voltage. Future studies will consider other geometries, higher charging voltages, different window materials, as well as other heat transfer mechanisms.
3.6 References


Chapter 4

TWO-DIMENSIONAL EFFECTS IN RADIANT HEAT FLUX ESTIMATION

4.1 Abstract

Chapters 2, and 3 showed the use of thin metallic films for the determination of heat flux at a solid surface. Depending on the duration of the event and gage design, it may be important to account for multi-dimensional heat conduction within the thin film substrate. Present chapter investigates the effects of two-dimensional conduction on the deduced radiative heat fluxes using an inverse algorithm. For comparison, the one-dimensional inverse technique, described in previous chapters, is also used. Both the one- and two-dimensional techniques are utilized to estimate the radiant heat flux from an electrothermal-chemical plasma jet. The plasma, initiated within a 3.2 mm diameter and 26 mm long polyethylene capillary by exploding a 3.6 mg thin copper wire, emerges into an open-air atmosphere as an underexpanded supersonic jet. The jet impinges over a stagnation plate equipped with thin-film platinum gages, whose temperature history serves as an input to the heat-flux estimation algorithm. Four different charging voltage levels are investigated, ranging from 2.5 to 7.5kV. While both algorithms capture the temporal variations of the radiative heat fluxes, two-dimensional model reveals the discrepancies between the two techniques as well as the range of applicability of the one-dimensional model.
4.2 Introduction

Transient heat-flux estimation typically employs surface temperature measurements followed by a suitable data-reduction scheme [1-2]. These schemes often utilize the measured temperature as a boundary condition, solve the heat conduction problem numerically, and estimate the temperature gradient at the surface. This procedure relies on the availability of a noise-free and a continuous boundary temperature [3-4]. Experimental data, being neither exact nor continuous, impose two-way instability in the solution. First, differentiation of the finite-precision experimental data sensitizes the estimated heat flux to measurement uncertainties causing solution instabilities [5-6]. Second, ill-posedness caused by the discreteness of the experimental data introduces non-uniqueness in the heat flux estimation [7-8]. While solution uniqueness can be influenced by the amount of acquired data, solution stability can only be achieved by a suitable mathematical treatment. Over the years, several techniques have been developed to deal with this stability issue. These techniques include: smoothing of either the discrete measurement data or the derivatives [5, 9], higher-order finite-difference schemes [10], filtering techniques [11-13] as well as inverse estimation technique. The inverse-based approach has shown several attractive benefits over other numerical techniques.

Inverse techniques, when implemented properly, can efficiently utilize experimental data. Except for a few simple and mostly one-dimensional (1-D) cases, where inverse problems can be solved analytically, the inverse procedure usually starts with a reasonable guess, solves a direct problem and forms a suitable functional using the difference between the calculated and the measured data. The functional is then gradually
optimized by an iterative improvement of the initial guess. Solution instability, caused by measurement noise, is circumvented by regularization. Regularization typically sets a stopping criterion for the optimization algorithm preventing minimization of the functional and thus, insulates the final solution from the measurement noise.

Inverse techniques can implement optimization and regularization in different ways. Early theories of inverse heat transfer problems, developed by Beck et al.[7], Alifanov[8] and Tikonov et al.[14] are now further extended and extensively applied by several authors including Ozisik and Orlande [15]. Inverse techniques were successfully implemented in conduction [16], convection [17], radiation [18], thermophysical property determination [19], as well as hyperbolic heat conduction problems [20]. In conduction heat transfer, inverse techniques can be used to recover unknown boundary or initial conditions [21]. Estimation of boundary conditions requires accurate information of thermophysical properties, temperature measurement within a region that is extremely sensitive to the unknown boundary condition, a suitable optimization algorithm as well as an effective regularization procedure to impose stability. Determination of unknown heat fluxes from surface temperature measurements at discrete time intervals can thus be modeled as an inverse conduction problem with unknown boundary conditions.

Taler [2] formulated an inverse heat conduction problem for estimating transient heat flux from surface temperature measurement using three different sensors: thin-film gage, thick-wall gage and thin-skin calorimeter. A 1-D inverse conduction model was employed to estimate the transient heat flux by the Stefan-Burggraf-Langford method. A smoothing technique, utilizing cubic spline or digital filtering, restricted the instability caused by measurement noise. The data-reduction complexity, however, was
compensated by an accurate and computationally efficient heat-flux estimation. Bezuidenhout and Schetz [22], Mota et al.[23] and Das et al.[24-25] also successfully implemented inverse techniques in estimating surface heat fluxes.

Walker and Scott extensively studied and compared different transient heat-flux estimation techniques using surface temperature measurements. They arranged available methodologies in three different groups: analytical, direct numerical and inverse techniques. 1-D conduction problems were formulated assuming typical transient variations of the surface heat flux. Based on a rigorous quantitative error analysis, it was concluded that inverse techniques, when properly regularized, provide the most accurate and stable solutions.

Despite the accuracy and stability of inverse heat flux estimation techniques, the assumption of one-dimensionality restricts their applicability. A deep thermal wave penetration coupled with, e.g., a highly localized heat flux imposed externally or imposed by the gage itself, may produce a substantial departure from one-dimensionality. Smith et al. [26] employed a two-dimensional (2-D) numerical model to examine the validity of 1-D assumption for heat-flux measurements in a gas-turbine application using thin-film gauges. Walker et al. [27-28] discussed a 2-D inverse approach and compared its performance with a 1-D technique in estimating heat fluxes during a shock-shock interaction. Following an earlier effort [29], they used a function specification method with suitable regularization. Using quantitative error estimation, it was concluded that the 2-D approach resolves steep spatial gradients of heat fluxes more accurately than the 1-D technique.
Large heat-flux levels occur during electrothermal-chemical (ETC) ignition of solid propellants. The ignition source is a high-temperature, high-pressure, metal-wire initiated, hydrocarbon capillary-sustained plasma jet. ETC ignition has confirmed its effectiveness over conventional chemical ignition methods [30-38], yet understanding of its complexity is only now beginning to emerge. Radiation constitutes one of the principal energy transport mechanism in ETC ignition [39]. Efforts of quantifying the relative importance of different energy transport mechanisms, therefore, include measurement and computation of transient radiative heat flux [24, 25, 40-47].

Measurement of radiant heat fluxes from an ETC plasma jet is often based on jet impingement on a surface, whose transient temperature is recorded via a surface-mounted thin film. The measured temperature serves as an input to a 1-D inverse data-reduction scheme for heat-flux calculation [24-25]. Surface temperatures are typically measured by narrow thin-film metallic gages placed on a low thermal conductivity substrate. The gage, connected with a constant current source, records the substrate’s surface temperature. Assuming 1-D heat conduction within the substrate below the gage with an unknown heat flux at one boundary and semi-infinite boundary condition at the other, an inverse conduction problem is formulated and solved. Despite the success of this technique when applied to low heat-flux levels, high heat-flux measurements require a substrate with a much higher thermal diffusivity to prevent gage failure due to excessive temperatures. Since the thermal wave penetration depth may be comparable to the gage width, the assumption of 1-D heat conduction in the substrate may be inaccurate. The data-reduction procedure should, therefore, be critically examined and suitably devised to address this issue.
The present study considers 2-D heat conduction within the substrate of surface-mounted thin-film gages subjected to high radiant heat-fluxes from an ETC plasma jet. The computational-experimental approach is described, and results from 1-D and 2-D inverse conduction techniques are compared. Experimental procedures and 1-D formulation utilizes a previously described procedure [24-25]. In this work, the thin-film platinum gages are mounted on polyimide or sapphire substrate, depending on the plasma energy levels. Narrow thin-film gages, coupled with high thermal conductivity and diffusivity of sapphire, may require consideration to 2-D heat conduction within the substrate. The study also investigates possible parameters influencing the 2-D effect within the substrate.

4.3 Apparatus and Approach

4.3.1 Plasma Generator

The pulse forming network (PFN) used for plasma initiation is discussed elsewhere in detail [24-25]. The PFN can be charged up to 10kV to yield a maximum energy storage of 9.6kJ. For the present experiment, four different voltage levels are studied: 2.5, 4, 5 and 7.5kV (0.60, 1.54, 2.40, and 5.40 kJ, respectively). The plasma chamber consists of a capillary, a fine copper wire, elkonite (copper-tungsten alloy: 30% Cu, 70% W) electrodes, and other nonconducting housing hardware. After being established, the plasma flows through an elkonite nozzle into the ambient open-air environment. Once evolved from the nozzle, the plasma impinges on a stagnation plate
located at a distance of 50mm from the nozzle exit. Heat-flux gages, covered by fused-silica windows, are placed on the stagnation plate. The details of gauge locations and window effects are discussed elsewhere [24].

### 4.3.2 Heat Flux Gage Design

Thin-film platinum (80nm thick) sputtered on polyimide (50µm thick) was used for deducing the transient variation of the radiative heat flux for a 2.5kV charging voltage. For higher charging voltages, platinum (80nm) was sputtered on sapphire (500µm thick). These gages are 0.25mm wide and 12mm long, suggesting that three-dimensional heat conduction effects are not important. A National Semiconductor’s LM134 constant current source, set at 3mA, powered by a 9V battery, is connected to the platinum gauge via 500nm thick sputtered copper leads. The gage was attached to a SS304 substrate through a transfer tape. Additional details are available [24].

### 4.4 Data Reduction

A standard 1-D inverse approach, for which a semi-analytical solution is available, estimates the transient, absorbed radiative heat flux variation from the measured time-dependent surface temperatures. The model assumes that conductive transfer in the substrate is 1-D, that a perfect thermal contact is made between the platinum film and the substrate, and that thermophysical properties are constant. Based on the inverse approach described in detail by Ozisik [15], a numerical procedure was
developed. The governing equation along with the initial and boundary conditions are discussed elsewhere in detail [24-25].

The 2-D inverse data reduction technique discussed here is developed around a conjugate-gradient optimization procedure. A typical conjugate-gradient algorithm starts with a steepest descent scheme followed by a coupling of present and previous descent directions through a conjugate coefficient [48-50]. This technique, when applied to inverse conduction problems, generates three partial differential equations namely, direct, adjoint and sensitivity [51], along with appropriate initial and boundary conditions. The solution starts from an initial guess of the unknown. A suitably defined functional, incorporating the measured and the computed data, is then iteratively optimized by adding gradual correction to the initial guess. Adjoint and sensitivity equations are solved to determine this correction. The adjoint equation calculates the gradient of the functional, which in turn determines the descent direction. The sensitivity equation utilizes the gradient to deduce the descent step size. In each iteration, all three equations are solved to generate a correction based on the descent direction and step size. Iterations proceed until the convergence criterion set by the regularization scheme is met [8, 15, 52].

In the present case, the 2-D inverse technique solves the following partial differential equation:

\[
k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) = \rho c \frac{\partial T}{\partial t}
\]  

\[
-k \frac{\partial T}{\partial x} = \begin{cases} q^*(t) & \text{at } x = 0, \ 0 \leq y \leq w \\
0 & \text{at } x = 0, \ w < y \leq d 
\end{cases}
\]  

(4.1)  

(4.2a)
\[ T = T_{ref} \text{ at } x \to \infty, t=0 \] (4.2b)

\[ \frac{\partial T}{\partial y} = 0 \text{ at } y = 0, d, \ 0 < x < \infty \] (4.2c)

\[ q^*(t) = \begin{cases} q^{j-1} \text{ at } x = 0, \ 0 \leq y \leq w \\ 0 \text{ at } x = 0, w < y \leq d \end{cases} \] (4.2d)

where \( q^{j-1} \) is the updated heat flux after the \((j-1)\)-th iteration. For the first iteration, \( q^*(t) \) represents the initial guess of the unknown heat flux. The above equations can be posed in the following dimensionless form:

\begin{align*}
\frac{\partial^2 \theta}{\partial x^*^2} + \frac{\partial^2 \theta}{\partial y^*^2} = \frac{\partial \theta}{\partial \tau} & \quad \text{for } 0 < x^* < \infty, \ 0 < y^* < \infty, \ 0 < \tau < \tau_f \\
-\frac{\partial \theta}{\partial x^*} = \begin{cases} q^*_*(\tau) \text{ at } x^* = 0, \ 0 \leq y^* \leq w^* \\ 0 \text{ at } x^* = 0, w^* < y^* \leq 1 \end{cases} & \quad \text{at } x^* = 0 \\
\frac{\partial \theta}{\partial y^*} = 0 & \quad \text{at } y^* = 0, 1, \ 0 < x^* < \infty \\
\theta = 0 & \quad \text{at } x^* \to \infty \\
\theta = 0 & \quad \text{at } \tau = 0
\end{align*}

(4.3) (4.4a) (4.4b) (4.4c) (4.4d)

where \( x^* = x/d, \ \tau = (\alpha t)/d^2, \ \theta = (T - T_{ref})/T_{ref}, \ q^*_*(\tau) = q^*(t)d/(kT_{ref}) \) and \( \alpha = k/(\rho c) \); \( w^* \) being the dimensionless gage half-width. Equation (4.3), along with the above initial and boundary conditions, describes only the direct problem. The solution to the subsequent sensitivity and adjoint problems is obtained by using a standard conjugate gradient technique and is discussed elsewhere [49][53]. The solution is regularized through the discrepancy principle [8, 15]. Discrepancy principle terminates the iteration
when difference between computed and measured temperature reaches the standard deviation ($\sigma$) of the measurement. While using experimental data, where $\sigma$ may vary from point to point, an average value of $\sigma$ is utilized.

Figure 4.1 shows the solution domain and the governing equation along with the boundary conditions. Considering the symmetry of the problem, the solution domain is restricted to half of the physical domain, i.e., $y=0$ is the symmetry axis. Radiative flux is absorbed by the gage located between $y=0$ to $y=w$, over which the flux is assumed to be spatially uniform. It is also assumed that the substrate reflects or transmits the radiative heat flux that arrives between $y=w$ to $y=d$, keeping $w<y<d$ virtually insulated. Symmetry and zero flux are assumed along midplane at $y=0$ and at $y=d$, respectively, whereas semi-infiniteness contributes the boundary condition as $x \to \infty$. In absence of direct experimental evidence, previous observations [24-25] are utilized as a guideline for deducing the boundary conditions. Further rationale of this computational domain and boundary conditions are discussed elsewhere [26-27]. The solution domain remains the same for the direct, adjoint and sensitivity problems; the governing equations and boundary conditions are, however, changed in each problem. Additionally, to impose the condition of heat flux uniformity over the gage and an insulated surface elsewhere, the gradient is averaged over the gage width and forced to zero elsewhere.
4.5 Solution Methodology

Intermediate steps of the 2-D inverse technique require numerical solution of partial differential equations using the deduced initial and boundary conditions. The solution domain (Fig. 4.1) is discreteized using a fully implicit finite-difference scheme. The ADI technique, followed by tridiagonal matrix inversion by the Thomas algorithm, is then utilized[54].

Grid independence of the numerical solution is tested against three different grid sizes: 51×51, 101×101, 201×201. A 101×101 grid size is selected finally as further refining produces negligible improvement of the solution. Non-uniform grids are used, keeping denser grids near $x=0$ and $y=0$ lines, followed by stretching of grid size in
geometric progression. The time step is maintained below one-tenth of the minimum specified by grid Fourier number criteria[51].

Grid independence of the numerical solution is tested against three different grid sizes: 51×51, 101×101, 201×201. A 101×101 grid size is selected finally as further refining produces negligible improvement of the solution. Non-uniform grids are used, keeping denser grids near x=0 and y=0 lines, followed by stretching of grid size in geometric progression. The time step is maintained below one-tenth of the minimum specified by grid Fourier number criteria.

For the validity of semi-infinite solid assumption, boundary condition as $x \to \infty$ should satisfy the relation: $x \geq 4\sqrt{\alpha t}$, which for the non-dimensional equations becomes $x^+ \geq 4\sqrt{\tau}$. Present solution maintained $x^+ \geq 5\sqrt{\tau}$ for all cases. In addition to numerically generated temperature profile, the simulations also use experimental data from the heat-flux gages exposed to plasma jet of varying energy levels. The heat-flux gage width is 250µm and distance between two consecutive gages is 9.5mm; y=w is set at 125µm and y=d at 500µm, as a larger value of d failed to produce any appreciable improvement in estimation.

The CPU time for the 1-D problem is around 1.5 minutes for 501 input data points, when using a 3.6 Ghz P4 computer with 512MB SDRAM with LINUX operating system. CPU time for the 2-D problem depends upon the initial guess. Using the 1-D solution as a first guess, the CPU time is about 5 minutes. Starting from a random guess, the computing time may rise up to 30 minutes.
4.6 Thermophysical Properties

The temperature coefficient of the electrical resistivity of platinum was assumed to be linear over the temperature range from 20 to 250°C, and was measured as 0.002/K using a standard convection oven. This value is about 50% lower than the bulk value (0.00389/K). The thermophysical properties of substrates are tabulated in Table 4.1. The normal polyimide conductivity obtained by Kurabayashi et al. is used here, and other data were obtained from manufacturer’s manual[57].

Table 4.1. Thermophysical properties of substrate materials

<table>
<thead>
<tr>
<th>Substrate material</th>
<th>ρ (kg/m$^3$)</th>
<th>c (J/kg-K)</th>
<th>k (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyimide</td>
<td>1420</td>
<td>1040</td>
<td>0.25</td>
</tr>
<tr>
<td>Sapphire</td>
<td>3985</td>
<td>750</td>
<td>37.50</td>
</tr>
</tbody>
</table>

4.7 Discussion of Results

Figure 4.2 illustrates the accuracy of the developed 1- and 2-D inverse techniques in estimating the unknown surface heat flux based on numerically generated input data. For these results, the 2-D direct problem is solved with a known surface heat flux at $x^* = 0$, semi-infinite condition as $x^* \to \infty$ and insulated boundaries at $y^* = 0$ and $y^* = 1$. The heat-flux profile at $x^* = 0$ is maintained as

$$q^* = 1.0 \text{ for } 0 \leq y^* \leq 1$$ (4.5)
The direct problem determines the transient surface temperature data that serve as the input to the inverse algorithms for the heat-flux reconstruction. The 2-D direct problem is solved keeping only few cells in $y$-direction, thus producing a 1-D temperature profile. The computed surface temperatures are assumed as exact data generated from an idealized experiment. Clearly, for this particular formulation no formal regularization is required, and the inverse problem reduces only to the minimization of the relevant functional. Simulating with a steady and spatially uniform heat flux, it is readily observed that both 1- and 2-D inverse techniques estimate the heat flux accurately irrespective of...
the substrate material. Both formulations produce similar results here, as the problem itself is essentially one-dimensional.

The accuracy of any inverse approach, however, diminishes rapidly with the introduction of noise in the input data. To illustrate the performance of inverse techniques with noisy data, a Gaussian noise is imposed over the exact data. For this purpose, Gaussian random numbers of specified mean and standard deviations are generated from the random number generation function provided within a standard high-level computer language. A Box-Muller scheme is utilized for this purpose [58]. The zero-mean random numbers are then used to perturb the simulated experimental data in the following manner:

\[ Y^* \text{ (perturbed)} = Y^* \text{ (exact)} \pm \Gamma \sigma \]  

(4.6)

where \( Y^* = (Y - T_{ref}) / T_{ref} \), \( \sigma \) denotes the standard deviation of the Gaussian distribution and \( \Gamma \) indicates the confidence interval, which is set here as 2.576 to specify 99% confidence. The results of the simulations are shown in Fig. 4.3 with an assumed heat-flux profile of

\[ q^*(\tau) = 4.0 \tau (1 - \tau) \quad \text{for } 0 \leq y^* \leq 1 \]  

(4.7)

Solving the 2-D direct and inverse problems using the discrepancy principle as iteration stopping criterion, it is readily observed that, the estimation deviates from the exact with the incorporation of the simulated measurement noise. However, if the discrepancy principle is rejected altogether and the functional is minimized towards zero, the inherent instability of inverse problem produces unbounded error as shown in Fig. 4.3.
Fourier number ($\alpha t/d^2$)

Non-dimensional Heat flux ($q^*$)

$\sigma = 0.0001$, regularized
$\sigma = 0.01$, regularized
$\sigma = 0.01$, non-regularized

Figure 4.3. Performance of two-dimensional inverse algorithm with noisy temperature data.

Figures 4.2 and 4.3 proved the effectiveness of 1-D and 2-D inverse techniques in recovering spatially uniform unknown heat fluxes. Results from 1-D and 2-D techniques coincide in these cases. Practical applications, however, often encounter spatially varying heat-flux profiles creating a 2-D temperature field within the substrate. 2-D algorithms are thus required in these cases. Case studies in Fig. 4.4 show the results of imposing the following nonuniform dimensionless heat-flux profiles A and B in Table 4.2. The solution starts by solving the 2-D direct problem (Eqs. 4.3-4.4) with the given heat-flux profiles. The temperature profiles at $x^* = 0$ thus obtained are used as the input to the inverse algorithms. The 1-D and 2-D inverse problems are then solved to recover the
surface heat fluxes. No measurement noise is imposed, i.e., the functional is minimized without premature stopping. A $w^*$ of 0.25 is maintained for both 2-D direct and inverse problems. As illustrated in Fig. 4.4, the results show appreciable deviation of the 1-D from the exact solution as time progresses. The 2-D formulation, however, accurately recovers the original heat fluxes. The 2-D formulation, used in the present investigation, deviates from the standard conjugate gradient technique [15] in terms of spatial averaging and allowing evolution of certain variables only at specified regions. Figure 4.4, therefore, in addition of showing the limitation of the 1-D technique, validates the 2-D algorithm as well.

Table 4.2. Different heat flux profiles used in simulations; $q^* = 0$ for $w^* < y^* \leq 1$ in all cases.

<table>
<thead>
<tr>
<th>Flux Profile</th>
<th>$q^* (\tau)$ at $x^* = 0$, $0 &lt; y^* \leq w^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.0</td>
</tr>
<tr>
<td>B</td>
<td>$0.50 + 2.0 \frac{\tau}{\tau_{\text{max}}} \left(1 - \frac{\tau}{\tau_{\text{max}}}\right)$</td>
</tr>
<tr>
<td>C</td>
<td>$0.50 - \tau(1 - 0.50\tau)$</td>
</tr>
<tr>
<td>D</td>
<td>$0.50(1 - \tau)$</td>
</tr>
<tr>
<td>E</td>
<td>$0.50(1 - \tau^2)$</td>
</tr>
<tr>
<td>F</td>
<td>$0.50(1 + \tau^2)$</td>
</tr>
<tr>
<td>G</td>
<td>$0.50(1 + \tau)$</td>
</tr>
<tr>
<td>H</td>
<td>$0.50 + \tau(1 - 0.50\tau)$</td>
</tr>
</tbody>
</table>
Figure 4.4. Performance of one- and two-dimensional inverse techniques with spatially varying flux profiles.

Figures 4.5-4.8 illustrate the performance of 1- and 2-D algorithms in reconstructing the radiant heat flux from the hydrocarbon capillary-sustained plasma jet. Four different plasma charging voltage levels are studied: 2.5, 4.0, 5.0 and 7.5kV (0.6, 1.5, 2.4 and 5.4kJ of energy, respectively). The 2.5kV case uses a polyimide substrate, whereas the other cases utilize a sapphire substrate. The temperature profile, used as the input to the inverse algorithm, is also shown in the plots. For convenient comparison with previous works [24][25], plots are presented in dimensional form. Error bars placed at $\pm 2\sigma$ indicate the uncertainties in the experiment and data reduction, where $\sigma$ is the standard deviation from three repeated experiments. The differences between 1-D and 2-
D estimations are calculated; a parameter $e$, the relative estimation error, is defined below and its values are tabulated in Table 4.3.

$$e = \left( \frac{q''(2-D) - q''(1-D)}{q''(2-D)} \right) \times 100\%$$

(4.8)

The sapphire substrate exhibited substantial deviation (25%), while negligible 2-D effect observed in polyimide (6%). Table 4.3 indicates weaker dependence of $e$ with plasma energy levels than substrate material properties. Average $e$ also exceeds $e$ at maximum

![Graph showing radiant heat flux and temperature rise](image)

**Figure 4.5.** Performance of one- and two-dimensional inverse data-reduction approach for estimating radiant heat flux from a 2.5kV capillary plasma.

heat flux location in all experiments, indicating maximum $e$ does not coincide with maximum heat-flux level. Additionally, it is important to observe that both the 1-D and the 2-D formulations do recover the fluctuating components of the transient radiative heat flux. This is clearly revealed in Fig. 4.8. The fluctuating components are largely caused
by the highly compressible nature of the underexpanded supersonic jet and its interaction with the stagnation plate.

Figure 4.6. Performance of one- and two-dimensional inverse data-reduction approach for estimating radiant heat flux from a 4.0kV capillary plasma.

Figure 4.7. Performance of one- and two-dimensional inverse data-reduction approach for estimating radiant heat flux from a 5.0kV capillary plasma.
Figure 4.8. Performance of one- and two-dimensional inverse data-reduction approach for estimating radiant heat flux from a 7.5 kV capillary plasma.

Table 4.3. Relative difference between the 1-D and 2-D algorithms in estimated heat fluxes for different charging voltages and substrate materials

<table>
<thead>
<tr>
<th>Charging Voltage (kV)</th>
<th>Substrate material</th>
<th>$e$ at peak heat flux location (%)</th>
<th>$e$ averaged over 0 to 500µs, $e_{av}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>Polyimide</td>
<td>5.23</td>
<td>7.65</td>
</tr>
<tr>
<td>4.0</td>
<td>Sapphire</td>
<td>22.60</td>
<td>33.24</td>
</tr>
<tr>
<td>5.0</td>
<td>Sapphire</td>
<td>19.14</td>
<td>31.11</td>
</tr>
<tr>
<td>7.5</td>
<td>Sapphire</td>
<td>17.47</td>
<td>21.02</td>
</tr>
</tbody>
</table>

While both algorithms recover the essential transient features, the nature of the 2-D effect requires further investigation. The 2-D effect implies lateral ($y$-directional) heat conduction, which is neglected in the 1-D formulation. Lateral conduction in sapphire
exceeds that of polyimide due to about 100-fold increase in thermal diffusivity of the former (Table 4.1). The very property that endorsed sapphire for high heat-flux measurements may contribute to its higher 2-D effect. An optimum design of heat-flux measurement experiment, therefore, requires identification of all possible parameters and their relative roles in contributing to the 2-D effect. The non-dimensional governing equations (Eqs. 4.3-4.4) suggest that for noise-free input data, the estimated heat fluxes and consequently the 2-D effect will depend only upon $\tau, \tau_{max}, q^*$ and $w^*$. To investigate the relative roles of these parameters on $e$, a series of numerical experiments are performed imposing different flux profiles, gage widths and maximum Fourier numbers. Temperature profiles generated from the 2-D direct problem are used as noise-free input to both 1- and 2-D inverse problems. Resulting 2-D effects are calculated using Eq. (8) replacing $q''$ by $q^*$.

Figures 4.9(a) and (b) show the variation of the relative heat-flux error $e$ with $w^*$ and $\tau$ for flux profiles A and B (Table 2) with a fixed $\tau_{max}$ of 1.0. The figures clearly reveal nonlinear increase of $e$ with increasing $\tau$ and decreasing $w^*$. For the parabolic flux profile (B), $e$ maintains a moderate gradient up to about $\tau = 0.50\tau_{max}$ and rises sharply for $\tau > 0.50\tau_{max}$. This sharp rise can be correlated to the decreasing trend in flux level in that interval. Figure 4 showed, for profile B, after $\tau = 0.50\tau_{max}$ the difference between 1- and 2-D estimations remains almost constant. The heat flux itself, however, drops and consequently the 2-D estimation, delivering a very high $e$ that may rise up to infinity if the flux attains zero at $\tau = \tau_{max}$. Nevertheless, in the interval $\tau \leq 0.50\tau_{max}$ the difference of $e$ from flux profiles A and B remains within about 10%. The 2-D effect, therefore,
tends to increase exponentially with Fourier number for a given \( \tau_{\text{max}} \) and \( w^* \); a decreasing heat flux profile further escalates this tendency.

![Figure 4.9. Effect of Fourier number on relative error \( e \) for different dimensionless gage half-widths with a (a) constant heat flux profile, (b) parabolic heat flux profile.](image-url)
To understand the variation of $e$ with the nature of input flux profile, a series of simulations are conducted using several monotonically varying heat-flux profiles. Six different profiles (C-H), described in Table 4.2, are utilized for this purpose with a constant $w^*$ of 0.50. All simulations are continued up to $\tau_{\text{max}} = 1$. The resulting $e$-variations with $\tau$, along with input profiles, are plotted in Fig 4.10. The plot clearly reveals the sharp rise of $e$ with temporally decreasing fluxes, while a moderate and largely profile-independent $e$-variation for temporally increasing fluxes. For temporally decreasing fluxes, trends show that a lower heat flux produces larger $e$ at a particular $\tau$, and $e$ rapidly increases as flux approaches zero. For temporally increasing fluxes, however, $e$ depends largely upon the heat-flux gradient ($dq^*/d\tau$), and a lower gradient produces a larger $e$. In Fig. 4.10, gradients of flux profiles F and H varies linearly with $\tau$. However, gradient of profile F increases from 0 ($\tau = 0$) to 1 ($\tau = 1$), whereas that of profile H decreases from 1 to 0, intersecting each other at $\tau = 0.50$. Consequently, the relative error $e$ from flux profile F exceeds that of profile H up to $\tau \approx 0.60$, after which the trend reverses. However, for all six cases, a temporally increasing heat flux produces a lower $e$ than a temporally decreasing flux. Surface cooling experiments are, therefore, more prone to a 2-D effect than that of surface heating.
In many experiments, knowledge of the peak heat flux is of importance. Experiment duration also sometimes poses a critical issue in designing an experiment. A series of simulations with varying $w^*$ and $\tau_{\text{max}}$ are, therefore, conducted to address these questions. Results plotted in Fig. 4.11 show the variation of $e$ at the peak flux location with $\tau_{\text{max}}$. These results are generated with flux profile B. The 2-D effects are calculated at $\tau = 0.50\tau_{\text{max}}$ and consequently plotted against $\tau_{\text{max}}$. Results show linear increase of $e$ with $\tau_{\text{max}}$. A maximum Fourier number of 0.50 will produce a 2-D effect of less than 25% at the point of peak heat flux.

Figure 4.10. Effect of Fourier number on the relative error $e$ for different heat-flux profiles. Profiles C-E represent a temporally decreasing, whereas profiles F-H represent a temporally increasing flux.
Figure 4.11. Effect of maximum Fourier number on relative error $e$ for different gage half-widths. Errors are calculated at the peak of a parabolic heat-flux profile.

Figure 4.12 shows variation of $e$ at a particular $\tau$ with variable $\tau_{\text{max}}$. Simulations with flux profiles A and B are conducted and corresponding 2-D effects at $\tau = 0.10$ are plotted against varying $\tau_{\text{max}}$. Figures reveal the constancy of $e$ with $\tau_{\text{max}}$ and independence of $e$ on flux profiles for $w^* \geq 0.20$. With profile B, heat flux at $\tau = 0.10$ decreases with $\tau_{\text{max}}$, producing a slightly increasing $e$ (Fig. 12b). For a constant heat flux (profile A), however, $e$ decreases marginally.
Figure 4.12. Effect of maximum Fourier number on relative error $e$ for different gage half-widths. Errors are calculated at a Fourier number of 0.10 with a (a) temporally constant heat flux profile, (b) parabolic heat flux profile.
Results shown in Figs. 4.9-4.12 can serve as a guideline in designing experiments with thin-film heat-flux gages. Caution, however, should be exercised while using these figures or procedure for several reasons. First, these results utilized simulated temperature profile representing practically unattainable noise-free experimental data. Second, a real experiment can hardly produce a smoothly varying well-behaved transient flux profile. In the present experiment of plasma radiation, simulation with profile B predicts a 2-D effect of around 10% for sapphire and around 3% for polyimide, which are about 50% of the actual values shown in Table 4.3. A more realistic assumption of flux profile and noise level as well as a detail and quantitative error analysis will result in superior and more accurate design of an experiment.

4.8 Conclusions

Effects of 2-D heat conduction in estimating transient heat-flux profiles from surface temperature measurements are discussed. The major findings from this study are as follows:

1. Both 1- and 2-D inverse techniques accurately recover the essential transient features in the heat flux, which are largely caused by compressible effects on temperature and species distributions within the plasma jet.

2. The importance of 2-D heat conduction increases nonlinearly with Fourier number and is largely independent of the heat-flux profile.

3. 2-D heat conduction effects are more conspicuous for temporally decreasing heat-flux profiles than the increasing ones.
4. When measured at a fixed Fourier number, 2-D heat conduction effects remain largely independent of the maximum Fourier number as well as the nature of imposed heat-flux profiles.

The present study deals with the effects of data reduction techniques in quantifying radiative heat transfer from a capillary-sustained plasma jet. Future studies will consider the effects of thermophysical and radiative properties of the substrate, film and window materials as well as the effect of non-zero film thickness on the radiative heat flux estimation.
4.9 References


57. http://www.goodfellow.com

Chapter 5
PARAMETRIC STUDIES ON ETC PLASMA RADIATION

5.1 Abstract

Chapters 2, 3, and 4 dealt with experimental investigation of radiative heat transfer from capillary-sustained plasma discharge. Focus of the present chapter is to identify the effects of capillary and trigger wire materials, plasma energy level, plasma exit port to stagnation plate distance, trigger wire mass, and capillary diameter on the transient electrical characteristics, radiant heat flux, stagnation pressure, and material ablation during the plasma discharge. Experiments were conducted with nine different combinations of capillary and wire materials, four different energy levels ranging from 0.60kJ (2.5kV) to 5.4kJ (7.5kV), and four different positions of the plasma chamber with respect to the stagnation plate. The results suggest that the radiant flux increases nonlinearly as the plasma exit port approaches the stagnation plate, and at a given plasma energy level, higher ablation typically indicates higher stagnation pressure, lower radiant flux.

5.2 Introduction

Electrothermal-chemical (ETC) plasma technology has been successfully applied for soft x-ray and extreme ultraviolet generation [1] as well as in plasma thrusters [2]. ETC plasma also appeared as a promising tool for fast and repeatable ignition of solid
propellants [3-7]. It is generally agreed that the plasma-propellant interaction during ETC ignition involves a combination of several complex thermochemical processes. Efficient design and optimization of an ETC ignition system requires quantitative understanding of the plasma-propellant interaction mechanisms as well as the thermophysics of the ablative plasma jet [8-9].

In recent years, semi-analytical and computational fluid dynamic investigations of varying complexities have been proposed to understand plasma initiation and flow within the capillary, as well as its interaction with stagnation plate and propellant samples [10-26]. Several experimental investigations were conducted to characterize ETC plasma temperature, electron number density, stagnation pressure, and species concentration [27-35]. Considerable effort was applied to understand the role of thermal radiation during ETC ignition of solid propellant [36-38]. Radiative properties of ETC plasma as well as spectral radiative flux during plasma-propellant interaction were also calculated [39-41].

Experimental investigations successfully deduced average radiative heat flux from ETC plasma jet [42-43]. Transient radiant heat flux estimation, however, was not quite successful due to high level of electromagnetic noise [27]. Results, however, indicated that radiative flux level is quite high in typical ETC applications. Time–resolved UV-visible spectroscopy was also employed to quantify the radiative flux density [44-45]. Spectroscopic investigation revealed that long capillary with thick trigger wire results in high capillary ablation but low radiative flux [46-47]. Recent investigation showed that thin film platinum heat flux gage, combined with inverse data reduction scheme, can effectively estimate transient radiant flux from ETC plasma [48]. Numerical
investigations also matches the radiant flux estimated from thin film measurements [49] confirms same order of magnitude radiant flux level. Thin film heat flux gages were also quite successful in outlining the capillary and trigger wire material dependence of transient radiant flux [50].

Above discussion reveals that the present knowledge on the role of radiative heat transfer during ETC ignition is far from being complete. The discussion also indicates that quantification of transient radiative heat flux, stagnation pressure, ablation parameters, and electrical parameters for a wide range of plasma energy level and plasma exit port to stagnation plate distance, may provide useful information for understanding the physics of ETC ignition as well as benchmarking the mathematical models. In this context, this chapter outlines the results of a series of experiments leading to the parametric studies on radiant energy transfer during ETC ignition. Following the same procedure of Das et al. [48], present research utilizes 80nm platinum on sapphire heat flux gage along with a multidimensional inverse data reduction scheme [51]. This study investigated the dependence of electrical parameters, material ablation, stagnation pressure and radiant heat flux, with capillary and wire material combination, plasma energy level, and the distance between the plasma exit port to the stagnation plate. Three different capillary materials, namely polyethylene (PE), lexan (LE), and Teflon (TE) are combined with three different trigger wire materials namely, copper (Cu), aluminum (Al), and nickel (Ni), producing nine different material combinations [50]. Each material combination is studied for five different energy levels (2.5, 3.0, 4.0, 5.0, and 7.5kV), and four different distances (5.0, 25.0, 50.0, 75.0mm) between the plasma exit port to
stagnation plate. Additionally, the effects of trigger wire mass, and capillary diameter on plasma radiation are also investigated.

5.3 Experimental Apparatus, Approach, and Data Reduction

Previous chapters provide the detail description of the PFN circuit, experimental set up and procedure, data reduction technique, heat flux gage design, as well as the thermophysical properties of the capillary and wire materials [48, 50-51]. Table 5.1 summarizes the experimental parameters investigated in this chapter.

Table 5.1. Summary of PFN circuit, experimental setup, and independent parameters varied during the parametric study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacitor (µF)</td>
<td>192</td>
</tr>
<tr>
<td>Inductor (µH)</td>
<td>20</td>
</tr>
<tr>
<td>Maximum energy dissipation capacity of the PFN circuit (kJ)</td>
<td>9.6 (at 10kV charging voltage)</td>
</tr>
<tr>
<td>Pulse length (µs)</td>
<td>~250</td>
</tr>
<tr>
<td>Capillary dimension</td>
<td>Length: 26mm, diameter: 3.2mm</td>
</tr>
<tr>
<td>Capillary materials</td>
<td>Polyethylene (PE), Lexan (LE), Teflon (TE)</td>
</tr>
<tr>
<td>Trigger wire materials</td>
<td>Copper (Cu), Aluminum (Al), Nickel (Ni)</td>
</tr>
<tr>
<td>Window material, thickness, and radiative property</td>
<td>Fused silica (S1-UV, ESCO Products), one sacrificial 1.59mm thick, another 4.76mm thick; transparent in 170-3000nm wavelength range</td>
</tr>
<tr>
<td>Charging voltage (kV)</td>
<td>2.5 (0.60kJ), 4.0 (1.5kJ), 5.0 (2.4kJ), 7.5 (5.4kJ)</td>
</tr>
<tr>
<td>Plasma exit port to stagnation plate distance (mm)</td>
<td>5, 25, 50, 75</td>
</tr>
<tr>
<td>Trigger wire mass (mg)</td>
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</table>
5.4 Discussion of Results

One of the advantages of ETC ignition is its repeatability. During these experiments, it is noted that the use of the basic resistive-inductive-capacitive (RLC) PFN circuit yields highly reproducible data from the current transducers, pressure transducers, and heat flux gages. The measurement uncertainties are quantified by placing error bars at ±2σ, where σ is the standard deviation from three consecutive measurements. Electrical noise is most pronounced during the first 25µs, when the plasma is being formed within the capillary. Some additional noise occurs during voltage reversals, which occur because the PFN circuit is slightly under-damped. During these experiments, nine different capillary and wire material combinations were studied, charging voltages were varied between 2.5 kV to 7.5 kV, and the distance between the nozzle exit to the stagnation plate was varied between 5.0 mm to 75.0 mm. Effect of trigger wire mass variation was also studied at 5.0 kV charging voltage, for all other experiments, trigger wire mass was kept constant at 3.6 mg. As the detail discussions on the transient nature of current, voltage, pressure, temperature, and radiant heat flux for 2.5 kV charging voltage has been reported before [50], present discussion of results begins with some of the representative results on transient variation of the electrical parameters. The discussion then proceeds toward the transient variation in radiant heat flux, and stagnation pressure for different charging voltages as well as nozzle exit to stagnation plate distances. The dependence of peak radiant flux, and stagnation pressure on capillary diameter, and trigger wire mass are also reported. Additionally, tabulated summary of the experimental results shows the variation in electrical parameters, ablated mass, peak radiant flux, and
peak stagnation pressure with plasma charging voltages, capillary and wire material combination, and plasma exit port to stagnation plate distance.

Figure 5.1 shows the transient variation of electrical current, voltage, energy, and power across the capillary at 4.0kV charging voltage with TE capillary and Ni wire. The electrical power is calculated by multiplying the electrical current with voltage across the capillary. Energy calculation involves numerical integration of electrical power over time. Power calculation is necessary, as the plasma characteristics as well as the shock wave formation is assumed to be power, rather than energy, driven [8, 52]. Transient steps of the plasma formation process are marked in the Fig. 5.1. Points 1 and 2 show the first and second inflection points in the current as well as power plots, representing the fragmentation of the trigger wire, and the initiation of the ablative plasma, respectively. Electrical power reaches its maximum just before the electrical current maximization. Previous works showed that electrical resistance of plasma minimizes during the electrical current maximization [32]. Maximum electrical current across the capillary, therefore, suggests the presence of maximum number of charge carriers within the capillary indicating the maximization of plasma electron density. As overall charge neutrality is generally considered a reasonable plasma approximation [53], higher electron density also implies higher density of positive charge. A high current discharge, therefore, indicates high-density plasma. Rigorous analyses of the wire explosion and the plasma formation process are presented elsewhere [28, 54-55].
Figure 5.1. Current, voltage, power and energy discharged by the PFN circuit across TE capillary with 3.6mg Ni wire at 4.0kV (1.56kJ) charging voltage; different stages of plasma formation also shown here.

Figure 5.2 shows the relevant electrical characteristics for LE-Al combination three different charging voltages: 4.0, 5.0, 7.5kV (1.5, 2.4, and 5.4kJ, respectively). During the initial phase of trigger wire explosion, the electrical resistance within the capillary increases rapidly, resulting consequent increase in voltage and decrease in current. Thus, the voltage across the capillary attains its peak during the trigger wire explosion. The peak value of voltage is about the same as the plasma charging voltage. As the plasma forms and begins to flow through the capillary, the electrical resistance within the capillary decreases, reducing the voltage to a quasi-steady state. Finally, the voltage reaches zero at around 250µs when the PFN circuit completely discharges the
stored electrical energy. While the quasi-steady voltage across the capillary shows weak
dependence on plasma energy level, the electrical current across the capillary and
consequently the plasma density within the capillary increases rapidly with the plasma
energy level.

![Graph showing electrical current and voltage across the LE capillary with 3.6 mg Al trigger wire for 4.0kV, 5.0kV, and 7.5kV plasma charging voltages.]

Figure 5.2. Electrical current and voltage across the LE capillary with 3.6 mg Al trigger wire for 4.0kV, 5.0kV, and 7.5kV plasma charging voltages.

In this study, material dependence of electrical current and voltage across the
capillary are measured for 2.5, 3.0, 4.0, 5.0, and 7.5kV charging voltages. Material
dependence of the electrical parameters of 2.5kV plasma was discussed elsewhere in
detail [50]. In the present study, it is observed that prominent qualitative features of
material dependent behavior in electrical parameters remain unchanged with plasma
charging voltage. Figure 5.3 shows a representative plot of material dependent electrical
characteristics including electrical current, voltage, and electrical power across a PE capillary for 4.0kV plasma charging voltage. Three different trigger wires are utilized namely, Cu, Al, and Ni. The inflexion points in the current curves show the transition from current flow through the trigger wire to current flow through the plasma. As the magnitude of electrical current is an indicative of plasma density, Fig. 5.3 shows that Ni wire produces highest density plasma. In case of Ni wire, however, the plasma formation process ($t_3 - t_2$) is longer than Cu or Al trigger wires, possibly due to the higher boiling point of Ni. Conversely, Al wire, with the lowest boiling point, produces lower density plasma, but reaches the maximum density point quicker than other trigger wires. The variations in the transient electrical parameters are generally attributed to the differences in the thermophysical properties and molecular structures of the trigger wire materials, discussed in Chapter 3.

![Figure 5.3. Electrical power, current, and voltage across the PE capillary with 3.6mg Cu, Al, and Ni trigger wires for 4.0kV charging voltage.](image-url)
As the duration of the plasma formation process as well as the time taken by the ETC plasma to reach its maximum density varies with capillary and trigger wire materials, it is also expected that the time lapse between the triggering, and the plasma emergence from the capillary ($t_4$) as well as the plasma arrival to the stagnation plate ($t_5$) will also vary. As shown in Fig. 5.2, the wire explosion ($t_1$), initiation of plasma formation ($t_2$), and time taken by the plasma for reaching maximum density point ($t_3$) are captured from the transient electrical current data. To understand the parametric variations in $t_4$, and $t_5$, two photodiodes were placed: one below the plasma exit port, another below the stagnation plate, as discussed in Chapter 2. Experiments were conducted for different capillary and trigger wire materials for a wide range of plasma energy levels. The distance between the plasma exit port and the stagnation plate is kept constant at 50mm. While transient nature of typical photodiode signals are discussed elsewhere in detail [48], a summary of the experimental results, showing material dependent $t_1$, $t_2$, $t_3$, $t_4$, $t_5$, and maximum current ($I_{\text{max}}$), for 2.5, 5.0, and 7.5kV plasmas are shown in Table 5.2. Using the results from three consecutive experiments, the uncertainties in the tabulated data are found to be about ±5%. Analyzing the data listed in Table 5.2, it is readily observed that time taken for wire explosion ($t_1$), and plasma formation ($t_2$, $t_3$) are material dependent, but largely independent of the plasma energy level. As the energy level increases the maximum current and consequently the maximum plasma density increases. While plasma emergence from the nozzle ($t_4$) and arrival at the stagnation location ($t_5$) expedite with the increase in plasma energy level, time taken by the bulk plasma to travel between the nozzle exit to stagnation plate ($t_5$-$t_4$) remains almost constant.
Table 5.2. Variation in maximum current, and time taken after triggering for trigger wire fragmentation ($t_1$), initiation of plasma formation ($t_2$), attaining maximum density ($t_3$), ejection from nozzle ($t_4$), arrival at stagnation plate ($t_5$) with charging voltage and capillary-wire material combination; trigger wire mass = 3.6mg, plasma exit port to stagnation plate distance = 50mm

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<th>$t_2$ ($\mu$s) (±2.3%)</th>
<th>$t_3$ ($\mu$s) (±2.1%)</th>
<th>$t_4$ ($\mu$s) (±4.5%)</th>
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<th>$I_{\text{max}}$ (kA) (±4.3%)</th>
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<td>4.3</td>
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</tbody>
</table>
In Table 5.2, the decrease of $t_4$ indicates higher pressure buildup within the capillary with increasing energy level. The pressure buildup, however, is largely due to higher material ablation resulting same bulk plasma velocity. Table 5.3 shows the capillary and nozzle material ablation for 2.5 - 7.5kV plasma energy level. During the wire explosion and the electrical discharge the nozzle serves as the cathode electrode. Ablation of anode electrode is typically negligible with respect to the capillary and the nozzle ablation. While total ablation increases with the increase in plasma energy level, the capillary ablation gradually tends to dominate over the nozzle ablation. At a charging voltage of 2.5kV, capillary and nozzle ablations are almost equal, whereas at 7.5kV, capillary ablation is almost double to that of nozzle, irrespective of the capillary and the trigger wire material combination. Additionally, it is observed that ablation from TE capillary always exceeds that of PE or LE. Detail description of material dependent ablation characteristics and its relation with electrical parameters are discussed in Chapter 3.

Table 5.3. Variation in ablated capillary and nozzle masses with capillary and trigger wire materials as well as plasma charging voltages; trigger wire mass = 3.6mg.

<table>
<thead>
<tr>
<th>Capillary and wire materials</th>
<th>Capillary ablation (mg)</th>
<th>Nozzle ablation (mg)</th>
</tr>
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</tr>
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</tr>
<tr>
<td>Ni</td>
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<tr>
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</tr>
<tr>
<td>Cu</td>
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<tr>
<td>Ni</td>
<td>6.5</td>
<td>8.7</td>
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</table>
As ETC plasma possesses almost material independent bulk velocity, and material dependent density, it is expected that high-density plasma will produce higher stagnation pressure. Figure 5.4 shows transient variation of stagnation pressure, and radiant heat flux for LE-Al combination at 4.0, 5.0, 7.5kV charging voltages. During these experiments, nozzle exit port to stagnation plate distance is maintained at 50mm. Previous works showed that plasma temperature maximizes almost simultaneously with the electrical current [56]. It is also reported that for 2.5kV-50mm, and 3.0kV-75mm configurations, radiant fluxes attain their peaks almost simultaneously with the electrical currents [48]. Previous works, therefore suggest that plasma temperature and radiant heat flux will reach their peaks almost simultaneously. Combining Fig. 5.4, and Table 5.1, it is observed that for 4.0, and 5.0kV charging voltages, the radiant flux and electrical current maximizes simultaneously. This phenomenon, however, changes when stagnation pressure peak precedes the electrical current peak. The stagnation pressure typically starts to increase as the precursor shock reaches the stagnation plate, and maximizes as the plasma impinges on the plate. When the plasma jet impinges on the stagnation plate before electrical current maximization, it may deposit sooty material on the fused silica window, creating vapor shield effect, and thus underestimating the peak radiant flux [5, 47, 57]. Additionally, the impact of plasma on the window may initiate vigorous mixing, initiating different course of chemical reaction pathways. Figure 5.4 shows that both these phenomena possibly occur for 7.5kV plasma charging voltage. During the impingement of 7.5kV plasma, when the stagnation pressure reaches its maximum, the rate of increase of radiant heat flux suddenly decreases indicating the possibility of vapor shield effect. The vapor shield effect, however, is not sufficient not prohibit the rapid
increase of radiant flux, after a delay of about 20µs, when the second stage of chemical reaction occurs. Similar nature of transient radiant heat flux was reported earlier for 7.5kV-50mm PE-Cu combination [51]. Impingement induced multistage chemical reactions, leading to multiple heat flux peaks, are also shown for 5.0kV charging voltage.

Figure 5.4. Transient radiant heat flux and stagnation pressure for LE capillary, Al wire combination for 4.0, 5.0, and 7.5kV charging voltages; plasma exit port to stagnation plate distance is 50mm.
Previous studies reveal that depending on the capillary and wire material combinations, multistage chemical reaction, and consequent secondary heat flux peaks are quite common even at lower energy level plasmas [50].

As the distance between the nozzle exit to the stagnation plate is reduced, both the transient radiant flux, and the stagnation pressure increase nonlinearly, as shown in Figure 5.5. The results shown here are for TE-Ni combinations at 4.0kV charging voltage. Three different plasma exit port to stagnation plate distances are considered: 50, 25, and 5mm. When the distance is reduced to 5mm, the plasma jet reaches the stagnation plate quite early, initiating further mixing and consequent chemical reactions. The radiant flux, therefore, exhibits multiple peaks, and may have been underestimated due to vapor shield effect. At a distance of 5mm, pressure transducers suffer, and are often destroyed, from excessive convective and radiative heating. To protect the pressure transducers, several layers of adhesive tapes are utilized. The pressure transducers, therefore, possibly fail to capture some of the secondary peaks, exhibiting a gradual pressure variation with time.
Figure 5.5. Transient radiant heat flux and stagnation pressure at 4.0kV charging voltage with TE capillary and Ni wire combination for plasma exit port to stagnation plate distance of 50, 25 and 5mm.
Material dependence of transient radiant heat flux and stagnation pressure for 2.5kV plasma was discussed earlier [50]. Figure 5.6 shows a representative plot for 4.0kV-50mm plasma using PE capillary with Cu, Al, and Ni wires. In this case, Cu

Figure 5.6. Transient Radiant heat flux and stagnation pressure for 4.0kV charging voltage with PE capillary, and 3.6mg Cu, Al, and Ni trigger wire.
trigger wire develops higher heat flux and lower stagnation pressure than Al or Ni wires. In general, combining with Table 5.3, it is readily observed that, for a given energy level, higher ablation leads to higher stagnation pressure, and lower radiant heat flux.

To understand the variation in the transient radiant heat flux, and stagnation pressure with plasma energy levels, capillary and trigger wire materials, as well as nozzle exit to stagnation plate distances all the experimental results are summarized in Table 5.4. At a distance of 5mm, experiments are conducted only up to 4.0kV charging voltage. At this distance, when charging voltage is more than 4.0kV, pressure transducers suffers from overheating, and the fused silica window used in the heat flux gages are destroyed due to high pressure impact. Additionally, as discussed earlier, at a distance of 5mm the radiant heat flux are possibly underestimated due to the vapor shield effects. Table 5.2 suggests that the increase in stagnation pressure is significant when nozzle exit is placed quite close to the stagnation plate (~5mm). It is also observed that, as the energy level increases, the material dependence of radiant flux become quite significant. In most cases, LE-Al combination provides maximum radiant flux, while TE-Ni combination results in maximum stagnation pressure resulting possibly from high ablation.
Table 5.4. Variation in peak radiant heat flux, and peak stagnation pressure with varying capillary and wire materials, plasma charging voltages, and plasma exit port to stagnation plate distances; trigger wire mass = 3.6mg.

(a) Plasma exit port to stagnation plate distance = 75 mm

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<th>Peak stagnation pressure (bar)</th>
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(d) Plasma exit port to stagnation plate distance = 5 mm

<table>
<thead>
<tr>
<th>Capillary and wire materials</th>
<th>Peak radiant flux (MW/m²)</th>
<th>Peak stagnation pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.5 kV</td>
<td>3.0 kV</td>
</tr>
<tr>
<td>PE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>555.1</td>
<td>883.4</td>
</tr>
<tr>
<td>Al</td>
<td>567.5</td>
<td>901.4</td>
</tr>
<tr>
<td>Ni</td>
<td>484.7</td>
<td>751.7</td>
</tr>
<tr>
<td>LE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>565.3</td>
<td>907.8</td>
</tr>
<tr>
<td>Al</td>
<td>578.2</td>
<td>954.1</td>
</tr>
<tr>
<td>Ni</td>
<td>395.4</td>
<td>789.5</td>
</tr>
<tr>
<td>TE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>503.2</td>
<td>771.6</td>
</tr>
<tr>
<td>Al</td>
<td>517.4</td>
<td>809.7</td>
</tr>
<tr>
<td>Ni</td>
<td>333.1</td>
<td>703.2</td>
</tr>
</tbody>
</table>

In order to understand the effect of trigger wire mass on radiant heat flux, and stagnation pressure, a series of experiments were conducted with LE capillary and Ni wire at 5.0kV-50mm configuration. Trigger wire mass was varied between 3.6 to 25.2mg. Figure 5.7 shows that the radiant flux reaches its maximum when trigger wire mass is
18.0mg. After this point, radiant heat flux starts to decrease. The stagnation pressure, however, increases monotonically. While further experiments are necessary to understand the wire mass effect on ETC radiation, present experiment suggest that for a given energy level, and material combination, after a critical value of trigger mass the radiant heat flux will tend to decrease. Increase of stagnation pressure suggests that, denser plasmas are generated with the increasing trigger wire mass. This high density, however, is mostly contributed by the high trigger wire mass. It is possible that the dense plasma will create an optically thick medium for radiation transport, absorbing most of the radiation. Additionally, previous experiments [45] show that plasma temperatures are typically lower than expected when trigger wires are quite thick.

![Figure 5.7. Variation in peak radiant heat flux, and stagnation pressure with trigger wire mass, for 5.0kV, LE-Ni plasma jets with nozzle exit to stagnation plate distance of 50mm.](image-url)
Another important parameter in ablative plasma is the interior diameter of the hydrocarbon capillary. When the capillary diameter is increased, the exposed capillary area, that receives thermal energy from the exploding wire, increases. However, with the increasing capillary area, the distance between the trigger wire and the capillary interior also increases. In this work, a series of experiments were conducted at 4.0kV-50mm configuration, with TE-Cu and PE-Ni material combinations, containing 3.6mg trigger wire. Three different capillary diameters were utilized, namely 2.0mm, 3.2mm, and 6.4mm. The results, plotted in Fig. 5.8, clearly shows that, as the capillary diameter decreases both the radiant flux, and stagnation pressure increase. It is, however, also observed that at 4.0kV charging voltage, when capillary diameters are less than 2.0mm, cracks develop within the capillary. The tendency of crack development is quite common, especially in TE capillary. At higher charging voltages, therefore, structural integrity of the ETC gun should be carefully considered for selecting the correct capillary diameter.
5.5 Conclusions

Parametric studies on ablation-sustained electrothermal-chemical plasma jet are conducted. Particular emphases are placed on the measurements of electrical characteristics, ablation parameters, radiative heat flux, and stagnation pressure. Thin-film heat flux gages are utilized along with pressure, and current transducers. Three different capillary materials (polyethylene, Lexan and Teflon) were combined with three different initiation wire materials (copper, aluminum and nickel). All the experiments were conducted in an open-air atmosphere with a fixed pulse length (~250µs), and fixed
trigger wire mass (3.6mg). Plasma jet, formed within the hydrocarbon capillary by exploding a trigger wire, is allowed to impinge over a stagnation plate. Plasma exit port to stagnation plate distance is varied between 5mm to 75mm. Plasma charging voltages also varied between 2.5kV (0.60kJ) to 7.5kV (5.4kJ). Dependence of radiant flux, and stagnation pressure on trigger wire mass and capillary diameter are also investigated. The major findings from this study are as follows:

1. The Lexan capillary with Al trigger wire generates maximum radiant flux, whereas the Teflon capillary with Ni trigger wire generates maximum stagnation pressure.

2. In most cases, for a given energy level, high material ablation by the plasma leads to high stagnation pressure, and low radiant flux.

3. As the distance between the plasma exit port to stagnation plate is reduced radiant heat flux increases nonlinearly; stagnation pressure increases rapidly when the exit port is quite close (~5mm) to the stagnation plate.

4. Depending on the capillary and wire material combination, charging voltage, and plasma exit port to stagnation plate distance, radiative heating can be single- or multi-staged, the latter possibly involving near-surface recombination reactions.

5. For a given capillary and wire material combination, charging voltage, and plasma exit port to stagnation plate distance, the radiant heat flux reaches its maximum at a critical trigger wire mass; stagnation pressure increases with the increase in the trigger wire mass.

6. Smaller diameter capillary generates higher radiant flux, and stagnation pressure, but is more susceptible to high-pressure, high-temperature failure.
5.6 References


Chapter 6

CONFINED RAPID THERMOLYSIS OF DOUBLE-BASE PROPELLANT

6.1 Abstract

Understanding the role of ETC radiation during solid-propellant ignition requires understanding of the decomposition behavior of the propellants. This chapter describes thermal decomposition of two double-base nitroester propellants, namely transparent (carbon free) and black (contains 0.05% of carbon) JA2. These two compounds were studied using confined rapid thermolysis. Gas-phase decomposition products were analyzed using rapid-scan Fourier transform infrared spectroscopy and time-of-flight mass spectrometry. Thermal decomposition was performed within a constant volume inert atmosphere, at a heating rate of approximately 2000°C/s. Investigations were conducted for three different decomposition temperatures: 250, 270, and 300°C, with a fixed propellant mass of 0.50mg. For comparison, nitrocellulose samples were also decomposed under the same conditions. Analysis of the gas-phase species indicates differences in the decomposition pathways as well as the chemical kinetic parameters of transparent and black JA2. While lower temperature decomposition of the propellants produced different species, higher temperature decomposition produced identical species at different rates. Results suggest that the presence of a small amount of carbon accelerates of the thermal decomposition of this double-base propellant.
6.2 Introduction

Double-base (DB) propellants generally refer to a broad range of energetic materials consisting of two major nitroesters, namely nitrocellulose (NC), nitroglycerin (NG), with several stabilizers, plasticizers, and catalysts. Thermophysical properties, chemical-kinetic parameters, and consequently the ignition and combustion pathways of the DB propellants can be tailored by varying the composition of the constituents. The effects of compositional variation on the ignition pathways are generally investigated by thermal decomposition studies of the propellants [1]. Applying a specified heating rate to a small amount of propellant within a controlled environment, thermal decomposition studies identify the transient species generation and consequently the primary as well as secondary chemical reactions leading to propellant ignition. Thus thermal decomposition studies help to formulate the elementary and global reaction mechanisms used in numerical investigations [2], as well as to identify suitable catalysts for desired kinetic performance. Thermal decomposition studies may also determine the degradation pathway of the propellant and consequently help in suitable stabilizer selection. While the decomposition pathways of NC and NG, as well as the general framework of DB decomposition are quite well understood, it is also established that, due to compositional variations, DB nitroesters may show substantial variations in decomposition patterns [3-7].

A particular combination of NC and NG, known as JA2, is now widely used in gun and rocket propulsion [8-11] In addition to NC and NG, the JA2 propellant contains diethylene glycol dinitrite (DEGDN). Table 6.1 shows the chemical composition of JA2,
while Fig. 6.1 shows the chemical structure of the major components. Depending on the presence or absence of carbon, optical and consequently radiative properties of JA2 may vary, giving rise to two different types of JA2: black and transparent. Additionally, presence of carbon changes the microstructure of JA2. Recent research suggests that microstructural variation can greatly affect the ignition and combustion behavior of propellants [12]. Due to these variations in the radiative properties and microstructure, transparent and black JA2 may exhibit different ignition and combustion characteristics. Recent investigations indicate that transparent and black JA2 respond differently to radiation-dominated ignition mechanisms [13-15].

Table 6.1. Chemical composition of JA2.

<table>
<thead>
<tr>
<th>Constituents (% by mass)</th>
<th>Black JA2</th>
<th>Transparent JA2</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC</td>
<td>59.50</td>
<td>59.50</td>
</tr>
<tr>
<td>NG</td>
<td>14.90</td>
<td>14.90</td>
</tr>
<tr>
<td>DEGDN</td>
<td>24.80</td>
<td>24.80</td>
</tr>
<tr>
<td>Akardite II + MgO</td>
<td>0.75</td>
<td>0.80</td>
</tr>
<tr>
<td>C</td>
<td>0.05</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Radiative heat transfer plays an important role in electrothermal chemical (ETC) ignition [16-19]. ETC ignition system uses a high temperature (~30,000K), hydrocarbon capillary-sustained plasma (electron number density ~10^{23} m^{-3}) jet to ignite the propellant. Recent investigations reveal that transparent JA2 behaves quite differently than black JA2 during ETC ignition [14-15]. The ignition and combustion characteristics of transparent JA2 are found to be more favorable for ETC ignition. These observations led to an increased interest in transparent JA2. The low temperature decomposition patterns of transparent and black JA2 are also found to be quite different [20]. The synthesis and selection of suitable propellants, catalysts, and stabilizers for ETC systems, therefore, require further understanding of the behavioral differences of transparent and black JA2. Apart from the variations in radiative properties, microstructural variations can also modify the ignition characteristics. A careful investigation of the thermal decomposition pathways of transparent and black JA2 can be the first step to elucidate the leading to ignition and combustion.

Thermal decomposition behaviors of general nitrate ester monopropellants (RO-NO_2), and NC in particular, are well investigated [21]. It is generally agreed that the NC
decomposition pathway involves first-order O-NO₂ homolysis, consequent production of nitrogen dioxide (NO₂) and alkoxy radical (RO’), followed by the autocatalytic oxidation of RO’, and hydrolysis of nitrate and glycoside groups [22]. Volltrauer and Fontijn [23] and later on Kimura [24] utilized chemiluminescence analysis technique to investigate NC decomposition in the 25-150°C temperature regime. Merzanov and his coworkers [25], and later on Zenin [26] investigated NC decomposition for temperatures above 200°C. Brill and Gongwer [27] studied NC decomposition for a wide range of temperatures (50–500°C) using T-jump/FTIR spectroscopy at a heating rate of 600°C/s. In this study, they critically reviewed the previous decomposition results of NC. Despite numerous available studies on NC decomposition, the reason of the autocatalytic oxidation of RO’ is not convincingly identified [28]. Experimentally determined activation energy also shows substantial mismatch with the expected value, calculated from the O-NO₂ homolysis reaction. Recent research of Smirnov [29] outlined the present understanding of NC decomposition, and identified the unanswered questions of NC decomposition.

Thermal decomposition pathway of NG follows the similar O-NO₂ homolysis mechanism. Svetlov [30] used manometric methods to study liquid-phase decomposition of NG at 80–140°C. Warning and Krastins [31] conducted manometric, and infrared spectroscopy studies on NG at a temperature around 150°C. Roos and Brill [32] reported FTIR and Raman spectroscopic studies on NG at 400°C and 5 atm at a heating rate of 2000°C/s. From these experiments, several important decomposition species have been detected, and some global reactions are also suggested. Information about the
autocatalytic reaction, and absence of substantial NO\(_2\), however, are yet to be conclusively explained [31].

While DEDGN is an important constituent of many double-base propellants [33-34], gas-phase species identification from the thermal decomposition study of DEDGN is quite rare in available literatures. Pinchas [35] identified the FTIR spectra of DEGDN vapor, whereas Cohen and Lo [6] suggested a global reaction mechanism of DEGDN combustion based on experimentally measured heat of decomposition. Miller and Anderson [36] compiled available data to compute the linear burning rate of DEGDN. Beckstead et al. [37] also adopted a similar approach for numerical investigation for DB combustion.

As the present understanding of NC, NG, and DEGDN decompositions are quite inconclusive, decomposition mechanisms of DB propellants, such as JA2, cannot be clearly explained. Especially intriguing are the reasons of autocatalytic reactions, and the disappearance of NO\(_2\). Mass spectrometric analysis of DB propellant by Dauerman et al. [38] suggested presence of NO\(_3\), instead of NO\(_2\) at a propellant surface temperature of 200\(^\circ\)C. Phillips [39], however, questioned the claim of NO\(_3\) detection, considering that dissociation energy for C-ONO\(_2\) bond is much higher than that of O-NO\(_2\) bond. Several investigations [40-41] concluded that the generation of NO\(_2\) is from the reduction of NO\(_3\), with NO being the primary product of this reduction reaction, thus questioning the occurrence of the primary first order O-NO\(_2\) homolysis. Dauerman and Tajima [42] presented an excellent review of the literature. Robertson and Napper [43-44] suggested that NO\(_2\) could be detected when gaseous products are collected in a stream of CO\(_2\). Based on these studies, Fifer [7] concluded that NO\(_2\) is very sensitive to experimental
conditions, and that NO\textsubscript{2} can be detected in a cold inert environment that can prevent secondary reactions. Roos and Brill [32], however, suggested that the mechanism of NO\textsubscript{2} disappearance in nitroester decomposition might be a very complex phenomenon, since under the identical experimental conditions, high concentrations of NO\textsubscript{2} and CH\textsubscript{2}O are observed from nitramine decomposition.

With this partial understanding of DB propellant decomposition mechanism, variation in decomposition pathways with compositional or microstructural changes cannot be reasonably predicted and has to be determined experimentally. Cohen and Lo [6] studied different DB compositions and concluded that the variation in chemical-kinetic behavior with composition cannot be correlated in a simple way. They also emphasized the necessity of numerical modeling to understand the experimental results. Sadasivan and Bhaumik [45] also conducted similar studies on compositional variations in DB propellant. Verneker and Kishore [46] carried out differential scanning calorimetry, and differential thermal analysis experiments with DB decomposition at 200°C. Investigating block and powder forms of the same chemical composition, they detected considerable variations in the decomposition mechanisms. These studies indicate that structural, physical, or compositional differences in DB propellants may initiate different thermal decomposition mechanism. Additionally, available decomposition studies mostly used black JA2, while recent research shows that transparent JA2 can be a suitable candidate for future propulsion systems.

Based on the incomplete understanding of DB propellant decomposition, lack of experimental data particularly on transparent JA2 decomposition, and the increased interest in transparent JA2 for ETC propulsion, present research focuses on the
differences in the thermal decomposition behaviors of transparent and black JA2. Confined rapid thermolyses (CRT) of transparent and black JA2 were conducted in the temperature range of 250-300°C with a heating rate of 2000°C/s and a propellant mass of 0.50mg. For a better understanding of the acquired spectra, nitrocellulose was also decomposed under the same environment. Detected gas-phase species were analyzed through rapid scan Fourier transform infrared (FTIR) spectroscopy and time-of-flight (ToF) mass spectrometry.

6.3 Experimental Approach and Data Reduction

6.3.1 Experimental Setup

The technique utilized to study the products formed under rapid decomposition of a material is referred to as confined rapid thermolysis (CRT)/FTIR/ToFMS. Using this technique, the thermal decomposition is limited to a volume confined between two heated, parallel surfaces. By using a small sample size compared to the volume, it is possible to study liquids that may otherwise largely boil off rather than decompose. The setup is composed of a constant pressure chamber, a Bruker IFS 66/S FTIR spectrometer and a commercially available ToF mass spectrometer. A three-dimensional view of the chamber, including a cut that exposes the sample holder, is shown in Fig. 6.2. The sample holder is designed to be lifted by the bottom heater to enclose the sample between the two heaters. Two ports are provided on the chamber, one serves as an inlet to the purge gas and the other exhausts decomposition products and the purge gas stream. The constant
pressure chamber, resting on a rigid frame, has a height of 27.5 cm and an inner diameter of 5 cm approximately. The CRT/FTIR technique has been described in detail in a previous work [47].

Figure 6. 2. Three-dimensional view of the high-pressure thermolysis chamber, exposing the sample holder, upper and lower heater, and the ZnSe windows through which the modulated beam of the FTIR propagates.

The rapid thermolysis is achieved by using two heaters: a stationary top heater and a mobile bottom heater. In both heaters, isothermal conditions are established by using high-watt density cartridge heaters (Omega CIR-1014/120V) and controlled by proportional-integral-derivative (PID) controllers (Omega CN8500). Both heaters are sheathed in copper rods, 53 mm in height and 15.6 mm in diameter. There are two auxiliary systems, a pneumatic piston-cylinder (Motion Controls) for lifting the bottom
heater and a purge gas system. The purging system using an inert gas serves a dual purpose. One, it purges the chamber of the decomposition products and prevents recirculation of products into the path of the modulated FTIR beam, and two, it prevents oxidation of the copper rods at elevated temperatures. The temperature of the cartridge heaters is monitored and controlled by two 75 µm K-type thermocouples embedded in the copper sheaths of the heaters.

To achieve rapid thermolysis, defined as an event that occurs within 5 seconds, temperatures of above 400°C are used. The experimental procedure is as follows: the heaters are brought up to the pre-set temperature. Approximately 0.5 mg of the sample is placed on the sample holder. As shown in Fig. 6.2, the sample holder is a hollow cylindrical ring with a thin foil attached on top. Though it is possible to utilize different types of foils, an 11 µm thick aluminum foil is used to minimize conductive heat transfer resistance and thermal mass. The sample holder is then placed over the guiding tube for the bottom heater and the bottom heater is raised by the pneumatic piston-cylinder. The sample holder is brought in contact with the ring retaining an aluminum foil over the top heater. This ring also defines and seals a gap of approximately 300 µm between the two heaters. The final position of the sample holder and the two heaters is shown in Fig. 6.3. A rectangular slit, 8.25 mm by 300 µm, is left open in the gap for gases generated during decomposition of the sample to gain access to the FTIR beam or to the orifice port on the vacuum chamber.
6.3.2 FTIR Spectrometer

The gaseous products evolve into the FTIR beam passing through two ZnSe (or KRS-5) windows, which are offset by 0.313 inches from the center of the chamber, offering a spectral coverage of 500-10,000 cm$^{-1}$. This wide range is truncated using a germanium coated KBr beamsplitter and a mercury-cadmium-telluride detector to the mid-IR range of 600-5,000 cm$^{-1}$. The gases evolved during the thermolysis are detected,
identified and quantified using FTIR transmission spectroscopy. The spectra are acquired with a spectral resolution of 2 cm$^{-1}$ and a temporal resolution of 50 ms.

### 6.3.3 ToF Mass Spectrometer

A low-pressure chamber with identical heater configurations is utilized for acquiring the ToF mass information at a high temporal resolution. The ToF MS system (Model D-677 from R. M. Jordan, [www.rmjordan.com](http://www.rmjordan.com)) is equipped with a 1m flight tube and a 44 mm microchannel plate (MCP) detector. Here, the recharging of the MCP detector may limit the temporal resolution to about 1 ms. The vacuum system is differentially pumped using a Leybold DIP8000 diffusion pump in the first stage, a Leybold TW700 turbomolecular pump in the second stage, and a Leybold TMP151 turbomolecular pump as well as two Varian Starcell 75 ion pumps in the third stage; four backing pumps are also used. Typical pressures are $10^{-4}$ torr in the first stage, $10^{-6}$ torr in the second stage and $10^{-7}$ torr in the third stage. Molecular beam sampling from atmospheric pressure gases is performed using a 100 µm orifice plate attached to the first stage, a 1mm diameter Ni skimmer (manufactured in-house by electroplating) attached to the second stage and a vertically translatable 0.5×12mm$^2$ slit attached to the entrance of the third stage. A schematic is shown in Fig. 6.4. The distance between the orifice plate and the electron beam in the flight tube is 0.279m. Electron impact ionization is set at 70eV, resulting fragmentation of molecules, but allowing comparison with mass spectral and related databases [48]. The electron beam interacts with the molecular beam during a period of 3 µs, after which extraction of positive ions occurs as a 250V voltage difference
is applied between the grid plates; the overall potential is normally set at 2.5kV. Data acquisition at 1GHz is PC-based using the 8-bit PDA1000 PCI-board (www.Signatec.com), which has 256MB of on-board memory and a 3-dB bandwidth of 0.5GHz. The MCP output signal is inverted and amplified 3.5× using a THS3201 amplifier from Texas Instruments.

![Diagram of a 100 µm diameter orifice port](image)

**Figure 6.4.** Sampling of evolved gaseous products occurs via the 100 µm diameter orifice port located on the first stage of the vacuum chamber.

### 6.3.4 Data Reduction

In order to deduce species concentration from the acquired FTIR spectra, the present investigation utilizes the model developed by Kim et al. [49]. This model considers both line and band structures of molecular spectra in correcting the finite resolution of the spectrometer, and utilizes the HITRAN database [50] for acquiring the
radiative properties of possible decomposition products. The computational algorithm uses Levenberg-Marquardt nonlinear least-square optimization scheme to iteratively fit the measured spectral transmittance to their theoretical values.

While FTIR spectroscopy can accurately quantify transient concentration of the IR-active species, several decomposition products, such as O$_2$, N$_2$, H$_2$, are known to be IR-inactive. In this study, ToF mass spectrometer is employed to identify both IR-active and IR-inactive species. The numerical procedure for time-to-mass scaling, from the acquired ToF spectra, employs the expressions $m=a(t-t_0)^2$, where the two constants for each mass spectrum are obtained from known positions of helium and argon. Further details of experimental procedure and data reduction technique are available elsewhere [47-49].

6.4 Discussion of Results

The DB propellants black JA2 (JA2) and transparent JA2 (TJA2) samples were obtained from ATK Technologies and used without further chemical processing. Under standard conditions, both compounds were solids. While JA2 was found to be of a nearly black opaque nature, TJA2 was a yellowish translucent compound. A small portion of the samples, approximately 0.50mg, was carefully sliced and subjected to CRT. While thermolysis was found to occur for both compounds from temperatures around 200°C, significant differences among the thermolysis products were observed at temperatures around 270°C.
6.4.1 Thermal decomposition of JA2 and TJA2 at 270°C

Figure 6.5 depicts the gaseous decomposition products evolving from CRT of JA2 at 270°C and an inert atmosphere of N₂. Strong rovibrational bands from the oxides CO₂, CO, and NO are easily visible in the FTIR spectrum. Also detected are H₂O and formic acid, with a strong C=O stretch near 1770 cm⁻¹. Another species with a strong C=O stretch near 1750 cm⁻¹ is also present, with a high probability of being an aldehyde or a ketone. H₂CO is present, as its rovibrational features near 2,700 cm⁻¹ are visible. Three peaks in the region 1300-700 cm⁻¹ indicate the presence of the oxidizing agent HONO [51]. HCN and N₂O were found in minute quantities. The IR frequencies of the commonly occurring gaseous species are listed in Table 6.2. Though NO₂ is widely regarded as the product of the initiation step during the decomposition of both NC and NG, only small amounts were detected in the FTIR spectrum, as verified by numerous other experimentalists. The probable reasons behind the lack of significant amounts of NO₂ are discussed in detail in later sections.

![FTIR spectrum of species from rapid thermolysis of JA2 at 270°C and 1atm N₂.](image)
Table 6.2. Vibrational frequencies of experimentally observed gaseous products.

<table>
<thead>
<tr>
<th>Description</th>
<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>3657 (s), 1595 (s)</td>
</tr>
<tr>
<td>CO₂</td>
<td>3716 (w), 3609 (w), 2326 (vs), 741 (m), 667 (vs)</td>
</tr>
<tr>
<td>CO</td>
<td>2142 (vs)</td>
</tr>
<tr>
<td>NO</td>
<td>1876 (vs)</td>
</tr>
<tr>
<td>NO₂</td>
<td>2910 (w), 1621 (vs), 648 (w)</td>
</tr>
<tr>
<td>HCOOH</td>
<td>3570 (m), 2942 (m), 1770 (vs), 1105 (s), 638 (s)</td>
</tr>
<tr>
<td>H₂CO</td>
<td>2843 (vs), 2782 (s), 1746 (vs), 1249 (s), 1167 (s)</td>
</tr>
<tr>
<td>HCN</td>
<td>3311 (s), 2097 (w), 712 (vs)</td>
</tr>
<tr>
<td>N₂O</td>
<td>2457 (vs), 2217 (vs), 1302 (vs), 1275 (vs)</td>
</tr>
</tbody>
</table>

In order to corroborate the presence of the species detected by the FTIR during the thermolysis of JA2, and to identify ones that remained undetected, the results from CRT/ToFMS of JA2 at 270°C and an inert atmosphere of He and Ar are displayed in Fig. 6.6. Individual mass spectra were acquired at 1000 Hz, averaging ten spectra to provide a temporal resolution of 0.01s. Averaging ten consecutive spectra was found to provide a high degree of accuracy with the standard deviation of the intensities staying below a value of 5 units. The usage of high ionization potentials, in the order of 70 eV, leads to considerable fragmentation of the heavier molecules, thus rendering the interpretation of data somewhat difficult. However, this difficulty is overshadowed by the ability to compare the data with existing mass spectral databases available for a wide range of compounds.
Figure 6.6. Mass spectrum from rapid thermolysis of JA2 at 270°C and 1 atm Ar, He and residual air (average of 10 spectra).

The following prominent peaks were assigned in the representative spectrum: the peak at m/z = 44 was due to primarily CO$_2$, and to a smaller extent, N$_2$O; the peak at m/z = 30 was primarily NO and H$_2$CO; the peak at m/z = 28 was CO and fragmented H$_2$CO and HCOOH; the peak at m/z = 29 was fragmented H$_2$CO and HCOOH. The following smaller peaks were also detected: the peak at m/z = 46 was due to mainly HCOOH and NO$_2$, with the peak at m/z = 45 attributed to HCOOH too; the presence of HONO was confirmed by the peak at m/z = 47; the peak at m/z = 27 was mainly due to HCN. The group of peaks at m/z = 55, 56, 57, and 58 is most likely to be caused by higher aldehydes. However, clear identification of the compounds was difficult owing to the coincidence of the location of the possible fragments with gases having smaller molecular weights. The set of peaks at m/z = 71, 72, and 73 are possibly larger fragments from the NC ring formed during thermolysis of JA2.

In order to shed further light on the decomposition pathways of JA2, the species evolution profiles were extracted from the FTIR spectra acquired at 270°C and shown in Fig. 6.7. The species were found to evolve at a fast rate after an induction period of approximately 700 ms. The rate of desorption of CO$_2$, CO, and H$_2$O were found to follow
a similar pattern, that with two distinguishable peaks, an initial steep peak, followed by another one with a lower slope. However, the profile of NO, the only significant oxide of nitrogen among the decomposition products, lacked the initial sharp rise. As predicted by the FTIR spectrum in Fig. 6.5, the amounts of both HCN and NO$_2$ were small compared to the other species. The presence of two distinct peaks in the species evolution profiles of the majority of the gases suggests two distinct decomposition pathways occurring in the condensed phase. Before discussing these processes in further detail, it would be advantageous to study the decomposition products from the thermolysis of TJA2 under similar conditions.

![Graph showing species evolution from rapid thermolysis of JA2 at 270°C and 1 atm N$_2$.]

**Figure 6.7.** Species evolution from rapid thermolysis of JA2 at 270°C and 1 atm N$_2$.

CRT of about 0.5 mg of TJA2 was concluded within a short time-span of 4 seconds at 270°C and atmospheric pressure. The decomposition products detected and analyzed by FTIR spectroscopy are shown in Fig. 6.8. The major feature that was
immediately evident was the prominent peak at 1621 cm\(^{-1}\) due to NO\(_2\), compared to a very small peak among the species obtained from the decomposition of JA2. The strong peaks at 1650, 1277, and 841 cm\(^{-1}\), and the smaller peaks at 2970, 2913, 1457, 1009, 900, and 751 cm\(^{-1}\) were found to increase and diminish at a similar rate, denoting that they are likely formed in the same overall pathway. After comparison with the IR spectra of several gaseous aliphatic nitrate esters published by Roos and Brill [32], the peaks were found to be from NG. Besides copious amounts of NO\(_2\) and NG, smaller amounts of CO\(_2\), CO, NO, H\(_2\)CO, HCOOH, and H\(_2\)O were also present in the spectrum.

The differences between the decomposition products of JA2 and TJA2 were also mirrored in the ToFMS results obtained at 270°C and shown in Fig. 6.9. The dominant peak at m/z = 46 portrays the profuse amounts of NO\(_2\) generated during the thermolysis of TJA2. The peaks at m/z = 44, 30, and 28 were considerably shorter, indicating decreased quantities of CO\(_2\), N\(_2\)O, H\(_2\)CO, NO, and CO. HONO, as verified by the FTIR spectrum, was present in trace amounts. NG, which was detected clearly in the FTIR spectrum, though not immediately identified by a large peak at m/z = 227, was subjected
to heavy fragmentation. It was identified by the presence of the peaks at m/z = 30, 46, 73, 75, 76, and the cluster of peaks around m/z = 90. Figure 6.10 describes the species evolution profiles from the FTIR spectra of TJA2. Since it was not possible to quantify NG in the gas phase due to the lack of a suitably pure sample, and possibility of decomposition, the evolution was studied qualitatively. Contrary to the profiles obtained from the decomposition of JA2, shown in Fig. 6.7, NO₂, accompanied by NG, started to escape into the gas phase after a shorter induction period of 500 ms. With the decrease of NO₂ and NG in the gas phase, the smaller gaseous products, namely CO₂, CO, NO and H₂O, slowly increased in proportion. While NO was released from the condensed phase at a relatively slow rate during the decomposition of JA2, its rate of desorption was roughly similar to that of the other species in case of TJA2. Another significant difference between the Figs. 6.7 and 6.10 was the absence of the double peaks observed in the profiles of CO₂, CO, and H₂O. Smaller amounts of HCN were found later in the event, signifying secondary recombination reactions.

Figure 6.9. Mass spectrum from rapid thermolysis of TJA2 at 270°C and 1 atm Ar, He and residual air (average of 10 spectra).
Figure 6.10. Species evolution from rapid thermolysis of TJA2 at 270°C and 1 atm N₂.

From the thermolysis studies conducted, it is evident that the major disparity between the two DB propellants was the high concentrations of NO₂ and NG detected initially in case of TJA2. The initiation step during the decomposition of the family of nitrate esters, to which all the major components NC, NG and DEGDN belong, is generally assumed to be the homolysis of one of the O–NO₂ bonds to liberate free NO₂ and an alkoxy radical. After the initial formation of NO₂, it participates in a series of secondary reactions involving the chain rupture and subsequent oxidation of the carbon backbone in case of NC, and the scission of C–C bonds in case of NG. Prediction of an all-inclusive set of complex condensed-phase reactions by studying the evolution of smaller-molecular-weight species into the gas phase is quite challenging and beyond the scope of the present research.
In order to understand the multiple processes occurring simultaneously among the components of the DB propellants, NC was acquired and subjected to thermolysis at 270°C. The species profiles in Fig. 6.11 confirm that the secondary reactions are fast enough to generate CO\textsubscript{2}, CO, NO, and H\textsubscript{2}O at a rapid rate. Nonetheless, in case of TJA2, the rates of the secondary reactions were considerably lowered. This phenomenon can be attributed to the “cage effect” [52-53], observed in case of condensed-phase reactions. The NO\textsubscript{2} generated during the initial O–NO\textsubscript{2} bond scission, being trapped in the “cage” in the condensed phase, is forced to participate in a recombination reaction to regenerate the parent nitrate. As would be confirmed in section 3.2, the tendency of NO\textsubscript{2} to participate in the recombination reaction diminishes as its mobility increases with increasing the reaction temperature. Additionally, the initial bond-breaking step in the decomposition is considered to be an equilibrium process [27], lending further credibility to the lack of rapid secondary reactions in case of TJA2. Certain fraction of the NO\textsubscript{2} formed escapes into the gas phase, along with considerable amounts of the parent molecule, NG. The desorption of NG allows the initiation reaction to proceed in the forward direction, thus allowing the secondary reactions to take place to a certain extent, and hence explaining the slow release of CO\textsubscript{2}, CO, NO, and H\textsubscript{2}O. Conversely, during the decomposition of JA2, the NO\textsubscript{2} formed in the initial step is promptly reduced to NO and CO by micronized carbon, preventing its buildup in the condensed phase “cage” and driving the reaction forward. Besides, the carbon is also believed to behave as a catalyst [7], enhancing the decomposition of nitrate-ester propellants.
6.4.2 Thermal decomposition of JA2 and TJA2 at 300°

Although the decomposition characteristics of JA2 did not undergo any appreciable changes at higher temperatures, the thermolysis behavior of TJA2 underwent a drastic transformation to closely resemble that of JA2. Figure 6.12 shows a representative spectrum during rapid thermolysis of JA2 at 300°C and a pressure of 1 atm N₂. The previously found set of species at 270°C, larger quantities of CO₂, CO, NO, H₂CO, HCOOH, and H₂O, and smaller amounts of NO₂, and HCN, were found to be present in similar proportions. The mass spectra acquired at 300°C, though not displayed, bore a striking resemblance to the one taken at 270°C, and shown in Fig. 6.6. The species evolution profiles are portrayed in Fig. 6.13. As expected, the induction time recorded...
was reduced to 120 ms. The previously noted double-peak feature was found to have been further well-defined at the higher temperatures. Additionally, the amount of NO\textsubscript{2} in the gas phase was found to be comparatively larger.

Figure 6.12. FTIR spectrum of species from rapid thermolysis of JA2 at 300°C and 1 atm N\textsubscript{2}

Figure 6.13. Species evolution from rapid thermolysis of JA2 at 300°C and 1 atm N\textsubscript{2}.
As mentioned earlier, the FTIR spectrum of the gaseous products from CRT of TJA2 at 300°C, shown in Fig. 6.14, was analogous to that of JA2 under similar conditions. No new species were detected after comparison with Fig. 6.12. The strong rovibrational bands belonging to NG were no longer found in the FTIR spectra. The relative concentration of NO\(_2\) among the decomposition products was also significantly diminished. The results from the FTIR spectra were reaffirmed by the mass spectra, displayed in Fig. 6.15. An interesting observation noted from the species profiles, shown in Fig. 6.16, was that the relative proportions of the mole fractions of both NO and NO\(_2\) were higher than those seen during the decomposition of JA2. Furthermore, the rate of evolution of NO was faster, and comparable to that of CO\(_2\), CO, and H\(_2\)O, when contrasted against the results obtained from Fig. 6.13. The reason behind the early evolution of the smaller molecular weight species at higher temperatures for TJA2 was the breakdown of the “cage effect” discussed earlier, caused by the heightened mobility of the NO\(_2\) molecules generated by the O–NO\(_2\) bond scission of the nitrate esters. Also, NO\(_2\) was expected to participate in an oxidation-reduction reaction [54] rather than a recombination reaction at higher temperatures, thus initiating further secondary reactions. Though the exact cause of the rapid evolution of NO in case of TJA2, compared to JA2 was not apparent, an appropriate speculation can be put forward. In case of JA2, the evolving NO is susceptible to reduction by the carbon particles, leading to the formation of nitrogen and CO, thus lowering the rate of formation and the final concentration of NO in comparison to TJA2.
Figure 6.14. FTIR spectrum of species from rapid thermolysis of TJA2 at 300°C and 1 atm N$_2$.

Figure 6.15. Mass spectrum from rapid thermolysis of TJA2 at 300°C and 1 atm Ar, He and residual air (average of 10 spectra).
6.4.3 Thermal decomposition of JA2 and TJA2 at 250°C

At lower temperatures, the decomposition characteristics of both JA2 and TJA2 followed a similar pattern as those exhibited at 270°C. The FTIR spectra, separated by approximately 100 ms, of the gaseous products from the thermolysis of JA2 at 250°C are shown in Fig. 6.17. While the second spectrum is almost a duplicate of the spectra obtained from JA2 at 270°C and 300°C, the first one, taken early in the event shows a few weak rovibrational bands that indicate the presence of vaporized DEGDN [35]. The existence of the strongest band at 1140 cm\(^{-1}\) was obscured by other bands in its proximity, especially the peaks due to HONO. The mass spectra and the species evolution profiles from JA2, being similar to those obtained at 270°C, were omitted. The
FTIR spectrum of the thermolysis products of TJA2 in Fig. 6.18 were also proportionate to the results observed at 270°C, indicating an abundance of NO$_2$ and vaporized NG, as well as decomposition to a smaller degree. It is clear that the decomposition processes occurring at lower temperatures are essentially similar to those at 270°C.

Figure 6.17. FTIR spectra of species from rapid thermolysis of JA2 at 250°C and 1 atm N$_2$.

Figure 6.18. FTIR spectrum of species from rapid thermolysis of TJA2 at 250°C and 1 atm N$_2$. 
The summary of the above discussion on DB propellant decomposition is presented in Table 6.3. From this discussion, it is quite evident that the decomposition pattern of TJA2 (carbon free) is distinctly different than that of standard JA2 (0.05% of carbon), especially at lower temperatures. Further investigations are necessary to understand the reasons of these differences.

Table 6.3. Summary of the variation in decomposition patterns of JA2 with temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Black JA2</th>
<th>Transparent JA2</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>Rapid secondary reactions leading to CO₂, CO, NO, H₂O, HONO, H₂CO, HCOOH; smaller quantities of NO₂, and HCN.</td>
<td>Identical products, but production of NO, NO₂, and rate of desorption of NO are higher compared to black JA2.</td>
</tr>
<tr>
<td>270</td>
<td>Decomposition almost similar to that at 300°C.</td>
<td>Large quantities of NO₂ and NG vapor evolved initially; smaller quantities of CO₂, CO, NO, H₂O, HONO, H₂CO found later in the event.</td>
</tr>
<tr>
<td>250</td>
<td>Decomposition almost similar to that at 270°C.</td>
<td>Decomposition almost similar to that at 270°C.</td>
</tr>
</tbody>
</table>
6.5 Conclusions

Confined rapid thermolysis of transparent and black JA2 was conducted at three different temperatures: 250, 270, and 300°C with a heating rate of approximately 2000°C/s. Gas-phase species were analyzed using rapid scan FTIR spectroscopy, and ToF mass spectrometry. For a better understanding of the acquired spectra, similar experiments were also carried out with nitrocellulose. The major findings from this study are as follows:

1. both propellants produced substantial amounts of CO, CO$_2$, and NO during high temperature (300°C) decomposition,
2. unlike JA2 and nitrocellulose, lower temperature (250°C, 270°C) decomposition of TJA2 produces large quantities of NO$_2$ and NG vapor,
3. during lower temperature decomposition, species production rate of TJA2 is considerably lower than that of JA2 possibly due to cage effect,
4. decomposition pattern of JA2 closely follows that of nitrocellulose, and
5. global reaction and chemical kinetic parameters might be different for transparent and JA2.

As the modern combustion modeling is gradually shifting toward using elementary reactions instead of a single global reaction, present investigation should provide additional guidance for formulating elementary reaction mechanisms for DB propellants, in particular for transparent JA2. Further investigations are underway for understanding the behavioral difference of TJA2 and JA2 during radiative pyrolysis.
6.6 Reference


Chapter 7

RADIATIVE PYROLYSIS OF JA2 PROPELLANT

7.1 Abstract

This chapter describes an effort to study the ignition of the double-base propellant JA2 mentioned in the previous chapter. The goal was determine Go/No-Go ignition boundaries, that is, determine the time to a sharp pressure rise signifying ignition. The JA2 propellant was placed within a small constant-volume chamber, which was attached to the stagnation plate. The chamber was sealed, but had access to the plasma radiation. Measurements of pressure and gas-phase temperature within the chamber, as well as analysis of gas-phase decomposition products from the plasma exposed JA2 were performed. The results show, however, that the JA2 propellant failed to ignite under all the considered charging levels, although pressures and temperatures reached quite high levels within the constant-volume propellant chamber. The lack of ignition is in large part attributed to UV-photolysis effects of the various nitrogen oxide and oxygen containing hydrocarbons among the pyrolysis products.

7.2 Introduction

Recent investigations in electrothermal-chemical (ETC) propulsion have convincingly proved its effectiveness in solid-propellant ignition and combustion [1-3]. During ETC ignition, radiation precedes convection. Thus the early changes in the
propellant grain structure and initial propellant decomposition are due to radiation alone. Radiative heat transfer is, therefore, generally regarded as an important mode of energy transport in ETC ignition. Preliminary numerical and experimental investigations conducted by Wren et al. [4], Schroeder et al. [5], Beyer and Pesce-Rodriguez [6], identified color and grain-structure modifications in ETC radiation exposed JA2 propellant; exposure to both convection and radiation showed an increased burning rate of the propellant. These studies also concluded that the radiation effects are more intense for transparent propellant samples and shorter plasma pulses. Shorter plasma pulses also resulted in higher capillary mass loss. Further experiments by Taylor [7-8] revealed that a higher energy level, larger capillary, and thicker trigger wire combination produces significant capillary mass loss but negligible radiation effects, and that, in these cases, metal vapor condensation is the dominant mechanism of energy supply to the propellant.

To understand the effects of ETC radiation on solid propellants, Katulka et al. [9] exposed several energetic solids, including JA2, M9 (57.62% nitrocellulose, 40.02% nitroglycerin), M10 (97.64% nitrocellulose), and M30 (28.71% nitrocellulose, 22.02% nitroglycerin, 47.34% nitroguanidine), to plasma radiation. A thin Mylar film was utilized to block the convective contribution as well as ultraviolet radiation. The plasma exit port to propellant sample distance was fixed at 30.48 cm. Varying the electrical energy discharge between 17 to 70kJ (60 to 264MW), it was observed that radiative ignition is possible only for 70kJ (264MW) plasma. FTIR studies of unburned samples indicated chemical changes, and possible denitration of nitrate esters.

Further experiments, conducted by Beyer and Pesce-Rodriguez [10], gas-phase species from 20kJ ETC radiation exposed solid propellants were collected. In this study,
the plasma was generated within a 3.8mm thick, 19.2 mm diameter Lexan cylinder, and the propellant was placed within a 5ml gas-tight syringe, placed outside the Lexan cylinder. The Lexan plate protects the propellant samples from ETC convection. Radiative properties of the Lexan plate as well as the syringe wall were not specified. It was, however, expected that the Lexan cover would serve as a shield to the ultraviolet radiation. FTIR studies were conducted to identify the pyrolysis products confined within the syringe. Investigating black (contains 0.05% carbon) and transparent (carbon-free) JA2 propellants, it was observed that both samples generated significant amount of CO, CO$_2$, and CH$_4$ but no detectable oxides of nitrogen. This investigation also concluded that the presence of carbon in black JA2 produced no other effect than shielding the inner portion of the propellant sample from ETC radiation.

In an effort to further understand and explain the plasma-propellant interaction, White et al. [11], Williams and White [12], Li et al. [13-14], and Das et al. [15-16] attempted radiant heat flux, plasma species, and stagnation pressure measurements. These experiments identified significant radiant flux, and high stagnation pressure from the ETC plasma jet, as well as quantified the capillary and wire material dependence of the radiant flux, stagnation pressure, and material ablation. It was also concluded that keeping the energy level and pulse duration the same, more ablation typically results in higher stagnation pressure, and lower radiant flux. These experiments also supplied useful information for the numerical investigations conducted by Nusca et al. [17], and Porwitzky et al. [18].

Building upon the previous work of Beyer and Pesce-Rodriguez [6, 10], Li et al. [13-14], and Das et al. [15-16], this chapter describes an attempt to examine the effect of
ETC radiation on transparent and black JA2 propellants. Unlike previous efforts, these experiments expose propellant samples to the combined UV, visible, and IR radiation (170-3000nm wavelength range). The present research quantifies electrical parameters, stagnation pressure, as well as the transient radiant flux from the ETC plasma jet. JA2 samples, located in a constant-volume chamber, were subjected to the plasma radiation. Transient variation of the chamber pressure, temperature, and the species generated from the plasma exposed JA2 were determined using diagnostic techniques described in earlier chapters.

### 7.3 Experimental Approach and Data Reduction

The apparatus and approach, including the PFN circuit, plasma generator, heat flux gage design and locations, pressure and current transducer details, capillary and wire material properties, and data reduction schemes, are discussed elsewhere in detail [15-16, 19]. The electrical discharge circuit, for plasma generation, uses an 850µF capacitor, ensuring high-energy plasma discharge (42.5kJ maximum). A 26mm long polyethylene capillary and a 3.6mg aluminum trigger wire are used in the plasma generator. In this investigation transparent (carbon-free) and black (0.05% carbon) JA2 samples are exposed to ETC plasma radiation. Detailed chemical compositions, and molecular structures of these propellants are described in Chapter 6.

Figure 7.1 shows a cross-section of the constant-volume propellant chamber. The chamber contains a 6.4mm diameter and approximately 1.4 mm thick sample (75mg). Fused silica (highly transparent between 170-3000nm) window, placed in front of the
Figure 7.1. Experimental arrangement for radiative pyrolysis studies.

propellant sample, prevents plasma convection from reaching the sample. The same window is used for radiant heat flux measurements. Additionally, a Zerodur window, opaque for wavelengths below 385nm, is used to quantify the visible and IR radiation from the ETC plasma jet. During the plasma discharge, transient pressure variation within the closed chamber is measured using a Kistler pressure transducer. Additionally, 12µm, bare-wire, K-type thermocouples, procured from Omega Engineering, are used in a slightly modified chamber to capture the transient variation in the gas-phase temperature. A photographic view of this chamber and the thermocouple location is shown in Fig. 7.2. Although barely visible, the thermocouple has a time constant to typical convective heat transfer rates that is of the order of 1 ms. As shown in Fig. 7.2, the thermocouple is located just beside the propellant sample. To reduce the effect of direct ETC radiant
heating of the thermocouple, a thin aluminum foil (not shown in the photograph) is placed about 1mm above the thermocouple. The aluminum foil is very small and just sufficient to protect the thermocouple bead without significantly reducing the radiation exposure of the propellant.

Figure 7.2. 12µm K-type thermocouple and a transparent JA2 sample, placed within the propellant chamber.

In another configuration, a 37ml stainless steel collection cylinder was attached to the propellant chamber through the pressure transducer port. The purpose of the cylinder is to collect gas-phase products generated during radiative pyrolysis of JA2. During the plasma discharge, gaseous products from pyrolyzed JA2 are allowed to flow in the collection cylinder. A 5ml gas-tight syringe is utilized to collect the gaseous samples
from the cylinder. The gaseous samples are then analyzed in the FTIR/ToF spectrometer. Details of the FTIR/ToF setup, experimental procedures, and the data reduction schemes have been discussed elsewhere [20]. Before the radiation exposure of the propellant samples, the propellant chamber as well as the collection chamber is purged using a helium-argon mixture. In a gun cartridge, the propellant charge is most likely confined in an air environment. This experiment is, however, designed to understand the possible thermo- and photochemistry of JA2 pyrolysis. Helium-argon environment is, therefore, used to serve as an inert gas with a limited reactivity with the pyrolysis products. During the heat flux measurements, the nozzle exit to heat flux gage distance is maintained at 25mm. The same distance is maintained during pressure measurements, and radiant pyrolysis of JA2.

### 7.4 Discussion of Results

Figures 7.3 and 7.4 show the transient variation of the electrical current and voltage across the capillary, external stagnation pressure, temperature rise, and radiant heat flux. The radiant flux reaches its maximum before the precursor shock reaches the stagnation plate. After reaching the stagnation plate the shock front experiences small oscillations, as captured in the pressure plot. Numerical studies by Nusca et al. [17] also successfully captured this pressure oscillation. After the jet reaches the stagnation plate it expands laterally, and heat flux decreases rapidly. However, as the plasma impinges on the stagnation plate, the shock structure and associated high speeds produce turbulent mixing of the plasma species, followed by further chemical reactions and a second heat
flux peak. To quantify the UV radiation from the capillary plasma, a Zerodur window is used in front of the heat flux gages. Figure 7.4 also shows that the UV radiation constitutes about 90% of the total radiation, which is consistent with the previous numerical investigations by Kappen and Bauder [21].

![Figure 7.3. Transient variation of electrical current, voltage, and electrical energy conversion across the capillary for a 4.0kV (6.8kJ) plasma discharge.](image-url)
Figure 7.4. Transient variation of radiant heat flux, and stagnation pressure for a 4.0kV (6.8kJ) plasma discharge

Figure 7.5 shows the transient variation in propellant chamber pressure. When the JA2 sample is exposed to the ETC radiation, the chamber pressure rises quickly, prior to arrival of the precursor shock, due to pyrolysis products. The pressure then decreases rather slowly due in large part to heat loss from the pyrolysis products to the chamber wall. To ensure that the pressure rise is due to the JA2 decomposition alone, the experiment is repeated without the propellant in the chamber. The chamber pressure variation in this case, due to high-pressure impingement of the plasma jet and consequent heating of the inside air, is found to be negligible, but shows that some ringing within the transducer occurs. The pressure variation is quite gradual, and reaches a plateau at about 0.5ms, after which the pressure decreases slowly. Mass of the propellant samples was
measured before and after the radiation exposure. Originally, sample mass was 75mg for both the propellants. After a 4.0kV plasma exposure the samples show 2.9mg mass loss for black JA2, and 1.3mg mass loss for the transparent JA2. Additionally, slight color change occurred in black JA2, while the transparent JA2 samples showed clear structure of inside void formation within the propellant [5].

Figure 7.5. Transient variation of stagnation pressure within the propellant chamber when the propellant is exposed to 4.0kV (6.8kJ) plasma radiation.

During plasma radiation exposure of JA2 propellant, one 12µm bare-wire thermocouple is utilized to measure the transient variation in the gas-phase temperature. A thin aluminum foil is utilized to protect the thermocouple bead from much of the direct
exposure to ETC radiation. Thermocouple results, shown in Fig. 7.6, indicate significant
temperature rise within the chamber, especially for black JA2. Figure 7.7 shows an
enlarged view of the initial phase of transient temperature rise when the propellant is
exposed to 4.0kV plasma radiation. Several interesting features are observed from Figs.
7.6, and 7.7. First, for the first 400µs, the thermocouple output suggests that the
temperature within an empty chamber exceeds that of the propellant-containing chamber.
It probably means that the radiation is diffusely reflected by the walls of the Lexan
chamber, and then absorbed by the thermocouple. The propellant sample, however, is an
efficient absorber of the radiation. Second, when the chamber contains a propellant
sample, at about 340µs the rate of change of gas-phase temperature increases. Finally, at
about 420µs the gas-phase temperature of the propellant chamber exceeds that of the
empty chamber. It is, therefore, concluded that during the first 340µs the gas-phase
temperature rise is primarily due to plasma radiation only. At 340µs the exothermic
chemical reactions begin to dominate over the radiative heating from the plasma.
Additionally, a closer inspection of Figs. 7.4 and 7.5 show that at 340µs the radiant heat
flux reaches its second peak, the visible-IR portion of radiative flux reaches its maximum
as well as a secondary pressure peak appears within the propellant chamber.
Figure 7.6. Transient variation of temperature within the propellant chamber when the propellant is exposed to 4.0kV (6.8kJ) plasma radiation.

Figure 7.7. Initial trend of transient temperature rise within the propellant chamber when the propellant is exposed to 4.0kV (6.8kJ) plasma radiation.
Combining Figs. 7.6 and 7.7, it is observed that the pyrolysis products undergo significant additional chemical exothermic reactions to produce a significant pressure and temperature rise. The constant-pressure adiabatic flame temperature of JA2 is around 2800K at 150psig, and the mole fractions of major equilibrium products are: 0.37 of CO, 0.26 of H₂O, 0.13 of CO₂, 0.10 of H₂ and 0.12 of N₂. Additionally, visual inspection shows color change in the black JA2, and void formation within the transparent JA2. It is, however, also observed that the propellant samples fail to ignite. Possible thermochemical mechanisms responsible for significant temperature and pressure rise in the gas-phase but unsuccessful ignition of JA2 are discussed further.

While ETC ignition of solid propellants is a relatively new field of study, thermophysics and chemistry of solid-propellant ignition, in general, have been investigated for several decades [22-26]. It is generally agreed that solid-propellant ignition involves a combination of several complex processes, such as, energy transfer to the propellant by an external stimulus, condensed-phase decomposition, and propellant vaporization as well as subsurface, heterogeneous, and gas-phase chemical reactions. Understanding the relative importance of these processes as well as identifying a universal ignition criterion is yet to be achieved. In general, solid-propellant ignition theories are classified into three major groups: solid-phase ignition [27-28], gas-phase ignition [29-31], and heterogeneous ignition [32-33]. Several numerical models have been developed around each of these ignition theories. Proposed models differ from each other in basic assumptions, governing equations, interfacial thermophysics, and type of propellants as well as ignition criterion. In recent years, predictive capabilities of ignition models are significantly improved by replacing the usual global kinetic schemes with
elementary chemical kinetics [25, 34-35]. These recent models also combine solid-phase, gas-phase, and surface thermochemistry to identify the temporal evolution of the propellant flame, providing an accurate prediction of propellant ignition. Unfortunately, experimental investigations of propellant surface, and condensed-phase thermochemistry are extremely challenging, and may suffer from high uncertainties [36-41]. Validation of various ignition models as well as clear understanding of solid-propellant ignition criteria, therefore, still remains quite elusive.

Considerable efforts have also been employed to understand thermochemical mechanisms as well as ignition criterion during radiative ignition, in particular laser ignition, of solid propellants [31, 42-50]. Both numerical and experimental investigations [47-50] showed that solid propellants often failed to ignite when the incident radiant flux exceeds a critical limit. Based on a one-dimensional condensed-phase model, Harrach [50] argued that solid-propellant ignition occurs at the condensed-phase surface, when rate of change of propellant surface temperature by radiation absorption equates that by the condensed-phase exothermic chemical reactions. Based on this argument, Harrach showed that beyond a critical limit, high radiant heat flux possibly causes rapid vaporization of the solid propellant, impeding propellant ignition. Ohlemiller et al. [47] again confirmed that the critical heat flux limit increases with increasing pressure. Although Harrach’s model [50] successfully predicted ignition delays of several solid propellants, Ali et al. [51-52] showed that Harrach’s model might not be accurate if the gas-phase chemical reactions dictate the ignition procedure. Conducting a series of investigations on laser ignition of octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine (HMX), and 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB), Ali et al. [51-52] showed
that ignition may occur above the calculated critical flux level, although the slope of ignition delay vs. the incident heat flux curve abruptly changes at the critical point. While these experiments contradict Harrah’s model [50], the results can still be explained by a previous model, proposed by Pantoflicek and Lebr [53].

Based on the experimental investigation on ammonium perchlorate ignition, conducted by Fishman [54], Pantoflicek and Lebr [53] formulated the necessary criteria for radiative ignition of solid propellants. It was suggested that for self-sustained ignition to occur, solid propellants should simultaneously attain certain critical surface temperature, as well as certain temperature profile within the solid phase. Pantoflicek and Lebr [53], as well as Ali et al. [51] showed that the temperature profile criterion is satisfied when the thermal energy stored in the propellant condensed phase exceeds a critical limit. It is also showed that for lower incident heat flux, the critical energy criterion is easily satisfied, and the surface temperature criterion dictates propellant ignition. For higher heat flux, however, due to rapid vaporization at the propellant surface, the propellant fails to store sufficient energy in the condensed phase. For high heat fluxes, therefore, the critical energy criterion controls the propellant ignition. For HMX propellants, this critical energy is found to be around 6.0J/cm² [51]. For double base nitrate-ester propellants, specific radiative ignition criteria are yet to be convincingly established. It is, however, generally agreed that the condensed-phase exothermic reactions dictate the ignition of nitrate-ester propellants, especially during low heat flux situations [22, 24, 55-57]. Due to the inherent difficulties in condensed-phase diagnostics, published results on the critical values of temperature, radiant flux, or energy, necessary for JA2 ignition, are quite limited. Conducting a series of Crawford strand burner
experiments on transparent and black JA2 at varying pressure, Eisenreich et al. [58] estimated that ignition surface temperature of JA2 is around 400°C. It is also observed that the surface temperature for JA2 ignition is largely independent of pressure, and initial propellant temperature. Information about critical ignition energy of double-base propellants is, however, not available in the published literature.

Unlike laser ignition of solid propellants, ETC radiation exposures are characterized by a short exposure, a highly transient event, as well as high heat flux environment. High heating rates may cause rapid vaporization of the propellant. Additionally, the pyrolysis products recirculate within the propellant chamber, flow over the colder fused silica window, further reducing their temperature. Combination of these two effects may prohibit the propellant surface to reach the critical temperature as well as evolution of a favorable temperature profile within the condensed phase, impeding the radiative ignition of JA2. Further understanding of radiative pyrolysis of JA2 calls for accurate measurement of JA2 surface temperature as well as critical energy for radiative ignition of JA2.

Besides the thermal effect of ETC radiation on JA2, ETC radiation, especially the intense UV radiation, may initiate chemical reactions that are absent in standard thermolyis of JA2. To understand these chemical effects and further investigate the unsuccessful ignition of the plasma exposed JA2, FTIR/ToF studies are conducted on the gas-phase pyrolysis products. Figures 7.8 and 7.9 show FTIR spectra of gas-phase species generated during radiative pyrolysis of black and transparent JA2 using 4.0kV plasma. The figures clearly show that FTIR spectra remain qualitatively similar when black JA2 is replaced by transparent JA2 samples. Additional experiments are also
carried out to understand the variation in the gas-phase species composition with plasma discharge energy level. Results, shown in Figs. 7.10 and 7.11, reveal that variation in the plasma discharge energy level between 5.2kJ (3.5kV) to 8.6 kJ (4.5kV) does not yield any detectable qualitative difference in the gas-phase species. It is, however, observed that with the increase in the energy level, for transparent JA2, CO$_2$ concentration increases at the expense of CO. This indicates that, compared to black JA2, transparent
Figure 7.10. Variation in gas-phase species concentration with plasma energy level during radiative pyrolysis of black JA2.

Figure 7.11. Variation in gas-phase species concentration with plasma energy level during radiative pyrolysis of transparent JA2.
JA2 pyrolysis creates more oxidizing atmosphere, and, therefore, is more likely candidate for radiative ignition. Conducting experiments from an energy level of 2.66kJ (2.5kV) to 20.83kJ (7.0kV), it is, however, observed that none of the propellants ignite though both of them exhibit increased mass loss as the energy level increases. These findings of unsuccessful ignition are consistent with the previous works of Katulka et al. [9], and Beyer and Pesce-Rodriguez [10]. Previous studies, however, exposed the propellant samples only to the visible and IR radiation, and detected only CO, CO$_2$, and CH$_4$ in the gas-phase pyrolysis products [10]. Present investigation, on the other hand, exposes the propellants to UV, visible, and IR radiation, and detects a variety of gas-phase species other than CO, CO$_2$, and CH$_4$.

Previous investigations showed that ETC radiative ignition of JA2 are difficult to achieve unless the plasma discharge energy level is quite high [9]. While previous experiments blocked the UV radiation to reach the propellant, present work shows that ETC plasma delivers significant UV radiation (Fig. 7.4). The present research, however, reveals that, for moderate plasma energy levels, combined exposure of UV, visible, and IR radiation may not be sufficient for radiative ignition of JA2. It is also observed that quality and quantity of gas-phase species, generated during radiative pyrolysis of JA2, differs significantly from that in confined rapid thermolysis (discussed in Chapter 6). Unlike conventional conductive or convective heating, ETC radiation exposes the propellant samples to a wide range of incident wavelengths including significant UV radiation. It is possible that the small wavelength exposure of solid propellants may initiate combined thermo- and photochemical events that are not experienced in conventional ignition procedures.
Available studies showed that UV radiation exposure is not a favorable option for energetic material ignition. Yong and Lui [59] explored the use of broadband UV, visible, and IR radiation as ignition sources for common pyrotechnic compositions, including Mg/NaNO$_3$, Mg/NaNO$_3$/ZnO, and gunpowder. During this study, the UV flux (4.9W/cm$^2$) was less than IR flux (18.5W/cm$^2$), but the exposure time for the UV radiation (10s) was much greater than that of the IR radiation (0.2-1.0s). It was observed that total energy requirement for ignition decreases with the increase in the incident radiation wavelength. Furthermore, when the pyrotechnic compositions were exposed to UV radiation only, none of the samples reached self-sustained ignition, even though absorbed UV radiation exceeds the amount of energy absorbed during IR ignition. The reason of this intriguing observation was not quite clear, and attributed to energy delocalization within the interatomic bonds of the oxidants, impeding decomposition and subsequent reaction with the fuel.

Ahmad and his coworkers conducted a series of experiments to understand wavelength dependence in radiative ignition of energetic material [60-61]. Rigorous investigation on laser ignition of double-base and composite propellants showed that, unlike composite propellants, laser ignition of double-base propellant is primarily a photo-thermal process, and that the photochemical reactions are responsible for increased ignition delay of double-base propellants. Conducting the laser ignition experiments with visible (500nm) and NIR (780nm) lasers, it was concluded that photochemical reactions are possible in the visible range when visible radiation is assisted by thermal stimuli. It was also suggested that UV exposure of double base propellants would result in photodissociation and photofragmentation of molecules even without thermal assistance.
In subsequent work on laser ignition of standard pyrotechnics, Ahmad and Russell [61] again showed that ignition energy requirement decreases with the increase in incident radiation wavelength.

Wavelength effects on the ignition, combustion, dissociation, and decomposition of organic chemicals are studied only around the broad framework of photochemistry [62]. Photochemistry of general energetic materials, in particular nitrate esters, under varied thermophysical and chemical situations, are yet to be adequately addressed. Early investigations by Devore et al. [63] identified the wavelength effects on nitrocellulose decomposition and reported pronounced photochemical activity near 254, and 313nm wavelengths. More recent studies outline general nitrate ester photolysis pathways [64-65]. Furthermore, major nitrate ester decomposition products such as, NO₂, H₂CO, and HONO, are known to be strongly affected by the following UV-photolysis reactions [66-69]:

\[
\begin{align*}
\text{NO}_2 & \rightarrow \text{NO}+\text{O} \quad (\lambda \leq 410\text{nm}) \\
\text{H}_2\text{CO} & \rightarrow \text{H}+\text{HCO} \quad (\lambda < 330\text{nm}) \\
\text{H}_2\text{CO} & \rightarrow \text{H}_2+\text{CO} \quad (330\text{nm} < \lambda < 365\text{nm}) \\
\text{HONO} & \rightarrow \text{NO}+\text{HO} \quad (\lambda \leq 400\text{nm}) \\
(\text{HCO})_2 & \rightarrow \text{H}+\text{CO}+\text{HCO} \quad (\lambda \leq 334\text{nm})
\end{align*}
\]

Understanding the exact mechanism of the radiative pyrolysis of JA2 calls for a logical coalescence of the above photochemical reactions with the standard thermochemical pathways, described in Chapter 6. Unfortunately, until now, coupled photo-thermochemical analysis of JA2 decomposition and ignition is not available in
open literature. Low-temperature photochemistry of nitrate esters is extensively investigated to address the problems of long-term chemical storage and degradation [70-71]. Thermochemical effects are reasonably neglected here. Broad-based thermal decomposition studies of nitrate esters, without photochemical effects, are also available [72-73]. Ling and Wight [74] identified different decomposition pathways, leading to similar final products, during laser photodissociation and thermal pyrolysis of glycidyl azide polymer, and polyglycidyl nitrate. None of the available studies, however, systematically addressed the combined effects of photo- and thermochemical mechanisms during energetic material ignition or decomposition.

Primary products of nitrate-ester decomposition are NO₂ and CH₂O. UV-photolysis of NO₂ and CH₂O, which occurs abundantly in the earth’s atmosphere, is extensively studied within the general framework of atmospheric science [75]. In the earth’s atmosphere, after the initial UV-photolysis of CH₂O, O₃ combines with H to produce HO₂, and thus triggers further oxidation of the photolysis products. Also during slow photochemical degradation, presence of oxygen accelerates the degradation reactions [71]. The present scenario of JA2 decomposition and pyrolysis, however, greatly differs from that of the atmospheric photolysis or slow photochemical degradation. Due to low oxygen balance of JA2 itself, high-temperature decomposition of JA2 often results in a reducing environment, generating hydrocarbon products, such as CH₄, C₂H₂, and C₂H₄ [73]. Furthermore, atmosphere supplies strong oxidants, such as O₃, which is not available in a real gun propulsion situation or in a standard laboratory environment. It is, therefore, possible that, during ETC radiation exposure, UV-photolysis will steer the standard decomposition pathway of JA2 [76], to a different
direction leading to a reducing atmosphere, unfavorable for radiative ignition. Further research, leading to exact identification of this radiative pyrolysis pathway, is in progress and will be reported in due course.

7.5 Conclusions

Effects of ETC radiation on JA2 propellant have been studied. The present study concludes that

1. radiation alone cannot ignite JA2 for a typical ETC application with a moderate plasma energy level,

2. gas-phase products, generated during radiative pyrolysis of JA2, are different from that generated during confined rapid thermolysis, and

3. UV-photolysis may be responsible for the failure in JA2 ignition.

Further studies are underway to justify the UV-photolysis hypothesis.
7.6 References


Chapter 8

SUMMARY AND CONCLUSION

8.1 Summary

Experiments are conducted to investigate radiative heat transfer from an electrothermal-chemical (ETC) plasma jet and to pyrolyze double-base propellants from ETC radiation exposure. The ETC plasma formation is initiated by electrically exploding a trigger wire within a hydrocarbon capillary. In these experiments, the ETC plasma jet is allowed to impinge on a vertical stagnation plate. The stagnation plate holds the pressure transducers, and thin platinum film heat flux gages. Several other diagnostic tools, such as a high-speed digital camera and photodiodes, are placed beside the plasma jet to capture the plasma evolution and impingement transience. Transient electrical current and voltage across the hydrocarbon capillary are measured using Pearson current transducers. In another configuration, the propellant chamber, attached to the stagnation plate, is exposed to ETC plasma radiation. Several diagnostic tools are utilized to analyze the gas phase products, generated from radiative pyrolysis of transparent and black JA2. These include Kistler pressure transducers, bare-wire thermocouples, FTIR spectrometer, and time-of-flight mass spectrometer. During all these experiments, fused silica windows, transparent in 170-2500nm wavelength range, were utilized to prohibit convective flux to reach the heat flux gage or the solid propellant. To understand the spectral variation of radiative heat flux, limited experiments are conducted with a zerodur window that blocks
the ultraviolet radiation. The overall objective of this research is to augment the present understanding of the thermophysical and chemical processes involved in ETC ignition of solid propellants as well as to provide experimental data for numerical model validation. Particular focus of these experiments includes:

1. development of thin film heat flux gages, and corresponding inverse data reduction schemes to capture the transient radiant heat flux from the ETC plasma,
2. quantification of mass ablation, radiant flux, stagnation pressure, and electrical parameter variations with the capillary and wire materials, plasma energy level, plasma exit port to stagnation plate distance, as well as capillary and trigger wire material combination,
3. quantification of spectral variation, wire mass dependence, and capillary diameter dependence of radiant heat flux, and
4. measurement of gas-phase temperature, pressure, and species concentrations during radiative pyrolysis of transparent and black JA2 propellants.

8.2 Conclusions

Experimental investigations are conducted on radiative heat transfer from electrothermal-chemical plasma jet. Major findings from this investigation are as follows:

1. ETC plasma produces high radiant heat flux with significant ultraviolet radiation. The instantaneous magnitudes of the absorbed radiative heat flux
may reach $10^9$ W/m$^2$. Visible and infrared radiations are relatively smaller and important only during the later part of the event.

2. Radiant heat flux, stagnation pressure, electrical characteristics as well as material ablation vary widely with capillary and trigger wire materials. For a given input electrical energy, pulse length, and trigger wire mass, higher material ablation typically leads to lower radiant heat flux. High material ablation, however, increases the density of the plasma leading to high stagnation pressure.

3. Trigger wire mass as well as inner diameter of the hydrocarbon capillary may affect the magnitude of the radiant heat flux. Radiant heat flux decreases with increasing capillary diameter, and initially increases and then decreases with the increasing trigger wire mass. Stagnation pressure decreases with increasing capillary diameter, and increases with trigger wire mass.

4. During plasma-propellant interaction, radiation alone cannot ignite the solid propellant. Radiation, however, initiates several thermo- and photochemical events, which are not experienced in conventional ignition systems. Radiation induces in-depth heating in the propellant condensed phase, and possibly UV-photolysis in the gas- and condensed-phases of the solid propellant.

5. The gas-phase species, generated during ETC radiative pyrolysis of double-base propellants, are different from the species produced during rapid thermal decomposition of the propellants in standard condition. This difference can be attributed to the high temperature and pressure experienced during radiative pyrolysis within the confined volume of accumulated gases. Additionally,
radiative pyrolysis induces photochemical reactions, which are not present in conventional decomposition.

6. Thin film gages can be quite effective in convective and radiative heat flux measurements. The heat flux estimation technique, however, should be carefully crafted depending on the magnitudes of the incident radiative fluxes, thermal wave penetration depth, as well as the thin-film dimensions.
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