LOW FLUX RADIATIVE IGNITION STUDIES OF AMMONIUM PERCHLORATE COMPOSITE PROPELLANTS

BY

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Thesis

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ABSTRACT

The vast majority of propellant ignition data has been collected and studied for heat fluxes in the typical, intentional ignition range. However, when a propellant contained within a rocket motor case is exposed to low fluxes in hazardous situations, such as close proximity to a fire, unwanted ignition can also occur. These studies set forth to model and study the conditions of such a situation, including ignition time and temperature profiles as a function of several constant incident low heat fluxes.

A CO$_2$ laser was used as the radiant heat source for ignition of aluminized and non-aluminized AP based propellants. A piece of blackened aluminum foil was bound to the top of the propellant to simulate the rocket motor casing and the propellant-metal interface. Once ignition time data and temperature profiles were collected, theoretical models were developed to model the behavior of the propellants under these low flux conditions.

It was discovered that under these conditions the samples still roughly exhibited the classic -2 slope on a log time versus log flux plot. However, the ignition time did increase for the samples covered with foil, as expected, due to the absorptivity of the foil. The experimental temperature measurements during heating to ignition followed the classic transient, 1D, semi-infinite solid with constant heat flux condition temperature profile, and were theoretically modeled as such. The final ignition temperature of the surface of the propellant was much lower than expected for what was reported in many other higher flux, air-propellant surface condition studies. However, this ignition temperature remained consistent throughout all of the tests.
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CHAPTER 1
INTRODUCTION

1.1 Motivation and Background

The primary motivation for this study is that the vast majority of ignition time and temperature of propellant combustion studies are done for heat fluxes in the region of significance for practical rocket propulsion. These heat fluxes can range from the hundreds to thousands of Watts per square centimeter over a time scale on the order of milliseconds. However, in possibly hazardous situations a rocket motor can become exposed to lower heat fluxes for longer times that could potentially result in ignition. Safety issues, as well as other major concerns, would likely arise from such an unwanted situation.

One of the major difficulties of studying solid propellant combustion is that despite extensive studies and data, it still remains not possible to predict or reliably model the ignition behavior of a new propellant system. This is due in large part to the complexity of the fundamental physics and chemistry in even the simplest of systems of a homogenous sample subject to monochromatic radiation. This perhaps can explain the lack of data and experiments done outside the interested heat flux range for rocker motor igniters.

This particular study was set forth to model and better understand how the rocket motor system would respond to extended exposure times of lower flux radiant energy. The conditions in these experiments were modeled to replicate those conditions that would be found in a rocket motor experiencing a potentially hazardous low flux exposure.
condition, such as a close proximity to a fire. In such a case when the outside of the motor case is exposed to a heat flux, the ignition occurs at the hottest spot, located at the propellant/liner/case interface instead of the intended interior surface of the propellant grain. A liner was not used in this study, but the inclusion of the propellant being bonded to a confining surface instead of a gas (typically air) should capture the main physical properties of what happens at this interface. AP/binder and AP/binder/aluminum solid propellant compositions were used, as this is the general type of propellant used in many rocket motor applications.

1.2 Objectives

The overall objective of this study was to gain a better understanding of the combustion characteristics of solid propellants subjected to lower than typical, intentional ignition radiant heat flux levels, as would be introduced in hazardous situations. The specific objectives include:

1) Develop a system for modeling the propellant/case interface that would be indicative of the surface interface conditions in the practical, real life rocket motor application.

2) Determine characteristic ignition times for these low fluxes for both aluminized and non-aluminized propellant samples whose surfaces are both exposed to a gas (air) and with a layer of metal between the propellant and the heat flux source.

3) Determine ignition temperatures and experimental heating temperature profiles for propellants subjected to these prescribed conditions
4) Compare these experimental results to the data in the higher flux practical application range where the behavior of this type of propellant has been well studied.

5) Develop a theoretical model for the ignition time-flux and temperature-time profiles and compare it to the experimental data.
2.1 General Overview of Solid Propellant Combustion

It is undeniable that solid propellant combustion remains an extremely complicated system despite years of experimentation and modeling. It has been estimated that roughly one thousand chemical reactions can occur at the surface of the propellant during ignition. The vast majority of experiments use radiant energy as the stimulus for ignition rather than convective or conductive heat transfer. This is the case due to the fact that a particular heat flux can be chosen and applied to the propellant independent of environmental factors such as pressure, initial temperature, and chemical composition of the gas surrounding the propellant. There are some slight drawbacks to the use of radiant energy to ignite a propellant sample. These include the lack of a hot gas next to the igniting propellant surface and the non-opaque characteristic of the majority of propellant samples, which leads to interior heating of the sample. However, as long as these problems are accounted for, radiant energy remains the leader for propellant ignition in studies.

2.2 Effect of Heat Flux on Ignition Time Studies

Ignition time versus heat flux is typically best modeled on a log-log plot. This is due to the fact that straight line slopes develop in the high and low flux regions. It was noted that a slope of -2 develops in the low flux region, while a slope of -1 develops in the high flux region, with a sharp transition at some intermediate flux as seen in Figure 2.1.
This transition point was noted as the critical flux, but was not fully understood when it was discovered. It was later determined that this transition was due to a dual ignition criterion. As demonstrated in Figure 2.2, both a critical temperature and a critical energy must be met for ignition to occur. For levels of high flux the energy contained within the solid is limiting as this criterion must be met after the sample has already reached and exceeded the critical temperature. On the other hand, for levels of low flux the surface temperature is the limiting factor as the critical energy has already been achieved at this point. The point at which the critical temperature and critical energy are met simultaneously corresponds to the kink in the log time versus log flux plot where the slopes change from -2 to -1. It was expected that since this study dealt only with low flux levels that the ignition criterion for each test would be temperature limiting. Also, this study only corresponds to the lower, first light boundary because the flux is not removed during the test, suggesting that only surface temperature and not the energy criterion is applicable. However it was important to know that this point existed and could possibly explain data points that did not fit the -2 slope toward the higher end of fluxes tested.

2.3 Surface Absorption Assumption

In this study of radiant heating and ignition of propellants, as well as with the vast majority of other studies, an assumption of surface absorption (surface heat flux boundary condition) is invoked. While this assumption is commonly used and taken to be widely accepted, it is important to understand its validity and how experimental results can deviate from modeled trends when this assumption is inaccurate. It is acknowledged that radiation absorption is a volumetric phenomenon even in opaque solids. However, in
many previous studies this possibility has been either ignored or neglected. The effect of volumetric absorption and its influence on the surface absorption assumption was examined, and as a result, a new in-depth absorption parameter was found and defined as

\[ \beta_s = \frac{T_s - T_0}{q / (kK_a)} \] (2.1)

As seen in Figure 2.3, for \( \beta_s \gg 1 \) the surface absorption assumption is valid, whereas for \( \beta_s \leq 1 \) in-depth absorption should be considered. Since this study deals exclusively with low levels of radiant flux, the results should lie in the \( \beta_s \gg 1 \) region where the surface absorption assumption is valid. However, this in-depth absorption condition could help to explain deviation from the classic -2 slope on the log-log plot of ignition time versus heat flux.

2.4 Ignition Determination

What is defined by propellant ignition can vary from study to study as ignition is actually a process by which the propellant goes through three stages as it is heated with a constant flux. As seen in Figure 2.4, once a thermal flux is chosen and imposed on the propellant sample, a period of inert heating occurs. During this stage a thermal profile will form at the surface of the propellant, but there is no apparent change to the sample if the heat flux is removed. As the sample continues to heat up, a point of first gasification will occur and light will be emitted. If the heat flux is removed during this stage, the sample will not continue to burn and the only change will be in the section of the sample that has already burnt away. If the propellant sample continues to be heated it will reach a go/no-go ignition threshold, where the sample will continue to burn even when the heat flux has been removed. This is due to the fact that a reaction is able to be sustained
through the establishment of the thermal profile and sufficient stability of the flame. The location and relationship between the lines is a function of several variables, which include pressure and amount of flux. As it can perhaps be noted in Figure 2.4, these two lines converge at levels of low flux, where first gasification and complete ignition occur simultaneously. These processes are often considered concurrent at flux levels less than 200 W/cm². Since the incident flux in this study was always under this value, first gasification and complete ignition were assumed to occur at once, and this was to be defined at the ignition point.
CHAPTER 3
EXPERIMENTAL METHODOLOGY

3.1 Sample Preparation

Two different kinds of ammonium perchlorate (AP) based propellants (aluminized and non-aluminized) were prepared for experimentation. For the non-aluminized samples, a division was used of 86% by weight of AP and 14% by weight of the binder. Of the total weight of the AP, it consisted of 50% coarse AP (nominally 200 microns) and 50% fine AP (nominally 90 microns). The binder was made up out of 69.4% Polybutadiene R-45M, 0.6% HX-878 Bonding Agent (cyanoethylated polyamine-tepanol), 15% acrylic monomer plasticizer (2-ethylhexyl acrylate), and 15% isonate 143-I MDI curative (diphenymethane diisocyanate). This information is summarized in Table 3.1. In terms of the aluminized samples, the same percent by weight (14%) of the binder was used (69.4% Polybutadiene R-45M, 0.6% HX-878 Bonding Agent (cyanoethylated polyamine-tepanol), 15% acrylic monomer plasticizer (2-ethylhexyl acrylate), and 15% isonate 143-I MDI curative (diphenymethane diisocyanate)). The AP was reduced to 70% by weight of the total sample, but the same ratio was kept between 90 micron fine AP (50%) and 200 micron coarse AP (50%). Additionally, 16% by weight was added of Al: ValleyMet H-15 aluminum powder, atomized, nominally 15 micron size. These ingredient proportions are recapped in Table 3.2.

Each of the ingredients were carefully measured out on a Fischer Scientific XA Analytical Balance and placed in a strong plastic bag in a specific order. The first three ingredients of the binder (Polybutadiene R-45M, HX-878 Bonding Agent
(cyanoethylated polyamine-tepanol), acrylic monomer plasticizer (2-ethylhexyl acrylate)) were measured out first. Next, the AP was measured out and mixed with the first three ingredients of the binder. The order by which the coarse or fine AP was added did not matter, but in the prepared samples in this study, the coarse AP was always added first. If the Al: ValleyMet H-15 aluminum powder was to be added to the aluminized samples, it was added at this point, after the AP. At this time all the ingredients were thoroughly mixed in the heavy duty plastic bag until the mixture visually appeared to be homogeneous. Only at this point was the isonate 143-I MDI curative (diphenylmethane diisocyanate) weighed out and added to the propellant mixture. This was done for safety precautions, as there was a slight risk if the curative had been added before the AP or the aluminum. The process of thoroughly mixing the propellant within the plastic bag was repeated until it again appeared visually homogeneous.

The propellant sample was now ready to be placed into a small Plexiglas box that had been previously constructed. The box measured 5 cm x 5 cm length by width and had a depth of around 2 cm. The box had an open side on the top for the propellant to be placed in. Before the sample was placed in the box, wax paper was placed inside as to aid in the removal of the propellant sample once it had been cured. Once the sample had been placed in the box it was pressed flat as to achieve a 5 cm x 5 cm length by width, with a depth of approximated 1.5 cm.

At this point, a 5 cm x 5 cm square piece of blackened aluminum foil was cut and pressed flat onto the top of the propellant sample. The foil had a measured thickness of 60 ± 5 microns. This was only done if it was desired that the propellant cover (blackened aluminum foil) be directly cured onto the top of the propellant. Samples, both covered
and uncovered, were then placed in a QL Model 10 Lab Oven for several days at 65 °C. Once the propellant samples had cured, as noted by their hardening, they were removed from the oven and brought back to room temperature (~27 °C).

Once the sample had cooled, the propellant sample was pulled out of the Plexiglas box and the wax paper was removed. A 5 x 5 grid was carefully measured and drawn out on the samples as to split the 25 square centimeter sample into twenty-five 1 cm x 1 cm samples. These samples had a typical depth of approximately 1.5 cm. A razor blade was then used to cut each of the individual samples. At this point the propellant samples were ready to be used in ignition time testing.

If the samples were to be used for temperature measurements additional steps were required. An uncovered (no blackened aluminum foil) 1 cm² sample was taken along with a 1 cm² square piece of the blackened aluminum foil that had not been cured directly to the sample. A Rdf Corporation type K chromel/alumel thermocouple, butt bonded, with a foil thickness of 0.00002 inches was also obtained for each sample that was to be tested. A propellant sample-thermocouple-blackened aluminum foil sandwich was then created, bonding together the three components with as little as possible epoxy as to eliminate any air gaps between the sample, thermocouple, and foil, but not to affect the thermophysical properties.

3.2 Experimental Apparatus and Configuration

The basic experimental setup remained common throughout all tests performed in this study, and is shown in Figure 3.1. A PRC-1000 1kW dc-excited, fast axial flow CO₂ (10.6 micron wavelength) was used as the radiant source. The laser produced a 16 mm
diameter circle cross section beam with a Gaussian (spatial) power distribution. A system of mirrors was set up so that the laser would be directed to the lenses on the workbench. The laser beam first hit a series of two ZnSe beam expander lens (4x) that expanded the beam’s diameter from 16 mm to 64 mm. The beam was then reflected off of a flat mirror and focused onto a SPAWR beam integrator. This integrator consisted of 49 flat 1 cm² mirrors that were specially oriented as to redistribute energy through an interference pattern. A spatially uniform beam profile was produced at a focal length of 25 cm. The ultimate incident beam on the sample was a square that was slightly larger than 1 cm. The concept behind these optics is better seen in Figure 3.2, although the figure is not to scale.

The propellant samples were placed in combustion chamber made out of Plexiglas, as shown in Figure 3.3. The dimensions of the combustion chamber were 20 cm x 20 cm x 50 cm. A hole was cut in the top of the combustion chamber in order to allow the laser beam to reach the sample since Plexiglas absorbs the CO₂ laser energy at the 10.6 micron wavelength. Additionally, a hole was cut in the side of the combustion chamber to allow an exhaust hose to be inserted. The combustion chamber was also raised from its base to allow air to flow up from the open bottom and out through the exhaust hose, which resulted in a reduction of the possibility of cross flow interfering with the combustion process. This system provided sufficient combustion product exhaust for the tests done in this study. This setup also allowed for all the tests to be done at or nearly at atmospheric pressure, which was important due to the fact that elevated pressure can significantly obscure the data.
3.3 Testing Procedures and Data Acquisition Methods

Before any tests were done, an Ophir 1000 W CO2/Nd:YAG steady power meter was used to calibrate the amount of laser energy lost from the lenses, reflections off the mirrors and primarily the integrator. The Ophir meter was water cooled and placed at the same location as the propellant would be during testing. Since the amount of energy leaving the laser was known and the amount of energy hitting the Ophir meter was also known, it could be calculated what percent of energy was lost through the optics. During all calibrations the amount of energy lost was always just around 50%.

There were two major areas of propellant combustion testing done during this study. The first area of study was that of the ignition times of the propellants under a low flux condition. Before any propellant samples were tested, a piece of burn paper was placed at the approximate location the laser would hit. From this point it would be known exactly where to place the propellant on the sample holder stand. The propellant would then be placed in its proper location and the laser set to the desired power setting for that particular test. Once behind a protective layer of Plexiglas, the laser was started with a remote start button as a timer was simultaneously started. As soon as the propellant ignited, the timer was stopped and the ignition time was recorded. This process was repeated for several flux levels varying between 7.5 W/cm² and 75 W/cm² for the uncovered non-aluminized, covered non-aluminized, and covered aluminized.

The second major area of study was that of propellant surface temperature during heating towards ignition. For these series of tests only samples that contained a type K thermocouple in between the blackened aluminum foil and the propellant surface were used. Using LabVIEW 6 on a Macintosh Powerbook G3 computer, a program was
written in order to obtain the temperature measurement from the thermocouple. A sampling rate of 1000 Hz was chosen for the program. The thermocouple leads were connected to a National Instruments DAQ board to an AI-16XE-50 DAQ Card, which connected the whole system to the computer. There were two different variations on the temperature tests. Since the ignition of the propellant sample would destroy the thermocouple during each test, the temperatures to ignition tests were limited to the few thermocouples available during testing. However, this was largely overcome by heating the sample with the laser until it neared ignition, letting it cool back down to room temperature, and the repeating the test with a different flux level from the laser. Since the ignition times were already known from the previous ignition time test, it could be known approximately how long the propellant sample could be heated at a particular flux before it ignited. The data from the temperature experiments were then written to a Microsoft Excel file where it could be analyzed.
CHAPTER 4
SYSTEM MODELING AND PROPERTIES

4.1 Properties

The thermophysical properties of each of the propellants main components (AP, binder, and aluminum) needed to be modeled as each component had separate property values, most of which had a temperature dependent variance.

AP is known to be a commonly used inorganic salt in many composite solid propellants and has been studied over a wide variety of temperature ranges. One interesting property of AP is that it features two crystalline phases in the propellant combustion temperature range. A transition from an orthorhombic crystalline phase to a cubic crystalline phase occurs at 513 K, although the transition can begin to be observed as early as 475 K. Consequently, the modeled thermophysical properties are known to change over this transition, although the thermophysical models used in this study have been developed to work for both phases of the AP. The following temperature dependent properties were used in this study to determine the properties. The specific heat in cal/g K of pure AP for all combustion temperature ranges is:

\[ c_{c,AP}(T) = 0.2612 + 0.45 \times 10^{-3} (T-T_{ref}) \] (4.1)

The thermal diffusivity of AP is known to decrease linearly in the orthorhombic phase and remain nearly constant in the cubic phase, and is modeled by the following relationships in cm²/s:

\[ \alpha_{ort,AP}(T) = 2.377 \times 10^{-3} - 4.55 \times 10^{-6} (T-T_{ref}) \] (4.2)

\[ \alpha_{cub,AP}(T) = 0.65 \times 10^{-3} \] (4.3)
The thermal conductivity is strongly nonlinear across the studied combustion temperature range. It can be roughly be modeled as being on average $1.0 \times 10^{-3}$ cal/ cm s K in the orthorhombic phase with a sharp drop off into the cubic phase until around 600 K where it remains nearly constant at $0.52 \times 10^{-3}$ cal/ cm s K.

Commonly used in aerospace propulsion and in some of the tests in this study, aluminum and its temperature dependent properties were also to be used. For the temperature ranges observed in this study, the following expression was valid for the specific heat of aluminum:

$$c_{c,\text{Al}}(T) = 0.2138 + 0.119 \times 10^{-3} (T-T_{\text{ref}})$$ \hspace{1cm} (4.4)

Although the thermal conductivity exhibits nonlinear behavior for the combustion temperature ranges, a linear relation has been developed that is sufficient for evaluating the thermal conductivity of aluminum in propellant combustion applications.

$$k_{c,\text{Al}}(T) = 0.486 + 0.277 \times 10^{-3} (T-T_{\text{ref}})$$ \hspace{1cm} (4.5)

In terms of the thermal diffusivity, it was acceptable in these experiments to take this value as a constant as 0.842 cm$^2$/s, which is the value of the diffusivity at an ambient temperature.

Perhaps the most important thermophysical properties to evaluate are that of the binder, since it is the first component of the propellant to ignite. The properties of the binder are often the most difficult to evaluate, since it is typically the smallest component by mass and can contain several different constituents. However, models have been developed for the interested temperature limits for the specific heat, thermal diffusivity, and thermal conductivity, respectively.

$$c_{c,\text{bn}}(T) = 0.46 + 0.588 \times 10^{-3} (T-T_{\text{ref}})$$ \hspace{1cm} (4.6)
\[
\alpha_{c,bn}(T) = 1.10 \times 10^{-3} - 1.50 \times 10^{-6} (T-T_{\text{ref}}) \quad (4.7)
\]

\[
k_{c,bn}(T) = 0.35 \times 10^{-3} - 0.143 \times 10^{-6} (T-T_{\text{ref}}) \quad (4.8)
\]

When properties of the different composite material needed to be combined to determine an overall property for the propellant sample, it was done on a weighted by mass basis. This was determined for aluminized and non-aluminized propellant samples by the following formula, where \( X \) is the desired thermophysical property:

Non-Al:

\[
X_{\text{propellant non-Al}} = 0.86 \times X_{\text{AP}} + 0.14 \times X_{\text{bn}} \quad (4.9)
\]

Al:

\[
X_{\text{propellant Al}} = 0.7 \times X_{\text{AP}} + 0.16 \times X_{\text{Al}} + 0.14 \times X_{\text{bn}} \quad (4.10)
\]

4.2 System Modeling

The system was modeled as a one dimensional unsteady (transient) conduction problem. Furthermore, it could be assumed that in all cases the propellant sample could be considered as a semi-infinite solid. This semi-infinite solid assumption was validated by using the following thermal propagation depth expression, in which it calculates the amount of time for the far (unexposed) end of the sample to feel a 1% temperature change.

\[
t_{1\% \ T} = \frac{(x/3)^3}{\alpha} \quad (4.11)
\]

All samples were on the order of 1.5 cm and the average thermal diffusivity of a propellant sample was approximately 0.002 cm\(^2\)/s. This gave an average thermal propagation time of 125 seconds, of which all but the lowest of fluxes had ignition times of under this mark. Slightly longer samples were used (2 cm) if the ignition time was to go beyond the previous mark because their thermal propagation time was estimated to be 222 seconds, which eclipsed the time of any of the tests.
It was also assumed that a constant heat flux from the laser was hitting the top surface of the propellant sample. While there were some fluctuations in the laser’s power output, it was never more than plus or minus a few Watts, and certainly not enough to invalidate the constant heat flux assumption. These two assumptions of a semi-infinite solid and a constant 1-D heat flux were particularly useful in that a widely used analytical solution for the temperature distribution throughout the solid had been formulated, the graphical model of which can be seen in Figure 4.1. The following equation for a constant surface heat flux in a semi-infinite solid was determined as the best model for this study:

\[
T(x,t) - T_o = \frac{2q^*_o \sqrt{\alpha t}}{k} \exp \left( -\frac{x^2}{4\alpha t} \right) - \frac{q^*_o x}{k} \text{ erf} \left( \frac{x}{2\alpha t} \right) \tag{4.12}
\]

Moreover, since the thermocouple was placed directly under the blackened aluminum foil, on top of the propellant (where x=0), the temperature distribution could further be simplified.

\[
T(t) - T_o = \frac{2q^*_o \sqrt{\alpha t}}{k} \tag{4.13}
\]

For the covered samples for which the temperature as a function of time was what known, the average heat flux to go through to the propellant sample could be solved for. Already knowing the incident flux upon the blackened aluminum foil, the absorptivity of the darkened aluminum foil could be found by dividing the recorded heat flux at the surface of the propellant by the known heat flux incident on the top of the blackened aluminum foil:

\[
\alpha(\text{absorbtivity}) = \frac{q_{\text{measured}}}{q_{\text{incident}}} \tag{4.14}
\]
5.1 Flux-Ignition Time Relationship

Three different kinds of propellant samples were tested on an ignition time versus constant heat flux basis. An uncovered, “bare” non aluminized propellant was initially tested as more of a control sample in this study before any covered samples were tested. Next, non-aluminized propellant samples with the blackened aluminum foil cover cured onto the propellant were tested. For the final set of tests, covered aluminized propellant samples were used.

In all cases, an error analysis was performed using the standard deviation from either the data trend line or theoretical line for both the ignition time and the incident flux. A standard deviation formula of

$$\sigma = \sqrt{\frac{\sum (x_i - m)^2}{n - 1}}$$

was employed to calculated the error bars that are seen in the ignition time-heat flux plots.

The uncovered propellant samples were tested with incident fluxes ranging from 5 W/cm$^2$ to 50 W/cm$^2$, with corresponding ignition times ranging from 1.5 to 87 seconds. Figures 5.1 and 5.2 show the data points with error bars in comparison to the theoretical -2 slope and the experimental data trend line, respectively. Additionally, Figure 5.3 shows the data set with both the theoretical and data trend lines. It can be seen that the experimental data gives a trend line with a slope of -1.72 in comparison to the theoretical -2 slope. There are several possible reasons that could explain this deviation from the
theoretical. The first, and perhaps most obvious, reason is the lack of total number of data points. The primary goal of this study was not to test these “bare” propellants, but rather the covered samples as this was more indicative of the real life situation these tests attempted to simulate. As a result, fewer tests were done and most likely a larger error developed in the experimental data trend line. Additionally, such factors as volumetric absorption, natural convection, and radiative emission could have skewed the data away from the theoretical slope, but with these limited tests it cannot be said for sure.

More extensive testing was then done on covered non-aluminized propellant samples with incident fluxes of between 75 W/cm² and 7.5 W/cm². The data set with error bars shows the relationship to the theoretical -2 slope in Figure 5.4 and the data set trend line in Figure 5.5. The comparison of these two lines is illustrated in Figure 5.6. Somewhat unexpectedly, a trend line with a slope of -2.19 developed from the experimental data. Deviation from the theoretical slope is typically not expected to be steeper, as a shallower slope can often be understood due to heat losses at the surface of the propellant (natural convection, volumetric absorption, radiative emission). However, upon consulting Figure 5.6, it can be seen that the difference in these two slopes is very minuscule and might have been thrown off by one or two data points. It would be expected that with further, repeated testing the data set trend line would more closely follow the theoretical -2 slope.

Finally, ignition time testing was performed on aluminized propellant samples. These samples exhibited a more sporadic behavior than the non-aluminized samples, therefore a smaller range of fluxes from 50 W/cm² to 15 W/ cm² were tested to make sure the experimental data was the most accurate. The data set with error bars are shown for
the theoretical -2 slope and the data set trend line in Figure 5.7 and Figure 5.8, respectively. Similarly to the other tests, the data set with both theoretical and data trend lines is shown in Figure 5.9. The data set gave a trend line with a slope of -1.75, which could be due to a number of factors. The overall wide fluctuations, as demonstrated by the larger error bars, could have undoubtedly contributed to a deviation from the theoretical trend. Additionally, as with the other tests, factors such as natural convection, volumetric absorption, and radiative emission that were not able to be quantified during this study may have contributed to the divergence from the theoretical trends.

5.2 Absorptivity and Pre-Ignition Temperature Profile

Incident radiant heat fluxes of 25, 20, 15, 10, and 5 W/cm² were applied to a propellant sample at room temperature. From the previous ignition time verses incident flux test it was known at approximately what time the propellant samples would ignite. This information was used to take the same propellant-thermocouple-blackened aluminum foil sandwich up to a temperature just prior to ignition. Even though these samples were not taken to ignition, a very good temperature profile did develop in the shorter time scale.

The first goal was to determine the absorptivity of the blackened aluminum foil using the measured temperature profiles. Using equation 4.13 the heat flux experienced by the propellant’s surface was calculated and the total absorptivity of the blackened aluminum foil was found by use of equation 4.14. The temperature dependent thermophysical properties in section 4.1 were used for the thermal conductivity and thermal diffusivity. The use of these temperature dependent properties instead of constant
properties would later be verified once absorptivity was determined. The average absorptivity was 0.17, which was slightly higher than the absorptivity of regular aluminum, as expected. The actual measured and theoretical temperature profiles for the covered, non-aluminized are shown in Figures 5.10-5.14. Once these experimental and theoretical profiles were plotted, it was determined that in fact the temperature dependent thermophysical properties more closely modeled the experimental data than the constant properties that equation 4.13 is based off of. It should also be noted that at some of the lower flux levels (10 W/cm², 5 W/cm²) it was determined from the experimental data that the laser power indicator was not quite correct since different flux levels (9 W/cm², 7 W/cm²) better modeled the experimental data.

5.3 Ignition Temperature and Heating to Ignition Temperature Profile

Two samples were then heated to ignition at incident fluxes of 20 W/cm² and 30W/cm² in order to verify that all of the propellant samples ignited at a limiting surface temperature. Theoretical temperature profiles were also developed using the same model as the previous pre-ignition tests. These temperature profiles are shown in Figure 5.15 for 20 W/cm² and Figure 5.16 for 30 W/cm². In each case the propellant samples ignited at approximately 240 ºC. This ignition temperature was much lower than a typical propellant ignition temperature of around 500 ºC. However, the theoretical model, previous tested ignition times, as well as consistency throughout all of the tests suggest that this 240 ºC ignition temperature may in fact be valid. One possible explanation for this lower than expected ignition temperature is that the thermal properties of the epoxy used to secure the propellant-thermocouple-blackened aluminum foil sandwich were not
accounted for. As little as possible epoxy was used in securing all of the components as to avoid this situation, but it still may have lowered the resulting measured ignition temperature.

Now that ignition temperature was known, the surface absorption assumption of section 2.3 could be verified. Using equation 4.13, with an initial surface temperature of 25 °C, a final surface ignition temperature of 240 °C, an absorption coefficient ($K_a$) of 333 cm$^{-1}$ (value for binder and AP at 10.6 micron wavelength of CO$_2$ laser), a thermal conductivity of 0.0042 W/cm K, and a high end heat flux of 30 W/cm$^2$, the in-depth absorption parameter comes out to be around 10. From the discussion in section 2.3, it can be seen that the surface absorption assumption should hold.

5.4 Theoretical Ignition Time versus Flux Behavior

Now that a non-aluminized propellant sample’s ignition temperature was measured, a true theoretical line could be added in the log time-log flux plots. Equation 4.13 was once again used as the heat flux was held constant, thermophysical properties were calculated as a function of temperature on an iterative basis, and time increased until the temperature reached the ignition temperature of 240 °C. This process was repeated for every level of heat flux tested. Both the experimental and theoretical data can be found in Figure 5.17, along with their respective trend lines. The theoretical trend line now had a slope of -1.96 due to the properties being evaluated on a temperature dependent basis. It was expected that this new slope be slightly less in magnitude than the original theoretical slope of -2, as predicted by equation 4.13.
CHAPTER 6
FINAL COMMENTS

As with any other detailed scientific investigation, the course of this study has proven to raise several more questions, both in terms of future works and also in the interpretation of the results. Perhaps the principal, not fully resolved relationship is between the absorptivity of the blackened aluminum foil and the ignition times between the covered and uncovered samples. The reported absorptivity of the blackened aluminum foil of 0.17 was chosen because it best fit the experimental results temperature profile when placed into equation 4.13 with temperature dependent thermophysical properties. However, an apparent discrepancy arises from this absorptivity in the time to ignition versus heat flux plots. It would be expected that ignition times would be similar for uncovered and covered samples when only the absorbed flux is considered, since it would take relativity just about the same amount of time to reach the proposed ignition temperature of 240 °C. Figure 6.1 shows the three sets of experimental data (uncovered non-aluminized, covered non-aluminized, and covered aluminized) on the same log time-log absorbed flux plot. The results show that it takes significantly longer for the uncovered samples to ignite as compared to the covered ones, and these lines do not match up as they would be expected to do. One possible scenario is that the uncovered samples have a higher ignition temperature, since the surface temperatures of the uncovered samples were not able to be recorded for this study. In many other studies, however, much higher ignition temperatures were reported, so this could be a definite possibility.
If it is assumed that all three sets of data have the same ignition temperature, then all three should line up in a log-log plot of ignition time versus absorbed flux. One way to attempt to explain this discrepancy was to manipulate the absorptivity value, as this would also shift the curves into the expected range of each other. The first possibility to look at was to change the value of the absorptivity of the blackened aluminum foil. The plot in Figure 6.1 was then manipulated by adjusting the absorptivity for the covered propellant samples (and therefore the absorbed flux) so that all three lines would relatively match up. The absorptivity that best characterized this feature was found to be 0.40, and is shown in Figure 6.2. However, this absorptivity did not correspond to the measured temperature profiles with the currently used theory and property parameters. It also was a bit higher than what would be expected for non-anodized aluminum at these temperatures.

The other possibility was to consider the manipulation of the uncovered propellant ignition time versus absorbed flux data. As seen in Figure 6.3, it was determined that for an uncovered propellant absorptivity of 0.50, all of the data points appeared to form a single trend line. One explanation for this is that from a previous study it was known that AP exhibits a unique property that its absorptivity reaches a value of around 0.5 at wavelengths slightly less than the 10.6 micron wavelength the CO₂ laser emits at. However, since there is only a peak at a wavelength less than 10.6 microns, this feature could extend to the 10.6 micron range and have an effect on the overall properties of the solid propellant, thereby explaining this shift in the data.

In addition to the discrepancies discussed above, several other factors were further considered that may have been intentionally or unintentionally neglected during this
study. One area of the theory that may have skewed the results is that temperature
dependent properties were used in an equation that was derived using constant properties,
although this gave a better shape to the temperature profile. However, it must also be
considered that these temperature dependent properties were being evaluated at the
highest temperatures in the system (since the thermocouple was located at the
propellant’s surface). It could be argued that it is possible that the properties should be
evaluated at a lower temperature that better reflects the in-depth cooler part of the
propellant sample. Perhaps, if this is the case, a full numerical temperature dependent
analysis may need to be performed.

It should also be considered that there may be some kind of physical system
condition that would alter the experimental results from the theory. One possibility is that
steady natural convection and radiative emission (which becomes more important as the
temperature increases) have a role in surface heat loss. While these are both likely factors
contributing to surface heat loss, their magnitude would be estimated at around 0.1
W/cm², which should not have a significant impact on the final results. One other
potential factor that was neglected was the possible impact of unsteady natural
convection. As the laser energy absorbed by the blackened aluminum foil starts heating
the foil and then the air around it, the once stationary air may become unstable after 10-
20 seconds, as newer and cooler air is brought in. These instantaneous heat transfer
coefficient values could be much higher than the typical steady values of around 10
W/m²K. While these factors were not believed to impact the results, it still was important
to consider their presence to confirm this belief or explain further deviations from the
expected data.
## Table 3.1. Propellant ingredients and mass proportions for non-aluminized propellant

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>% by Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Binder</strong></td>
<td>14%</td>
</tr>
<tr>
<td>Polybutadiene R-45M</td>
<td>9.716%</td>
</tr>
<tr>
<td>HX-878 Bonding Agent (cyanoethylated polyamine-tepanol)</td>
<td>0.084%</td>
</tr>
<tr>
<td>acrylic monomer plasticizer (2-ethylhexyl acrylate)</td>
<td>2.1%</td>
</tr>
<tr>
<td>isonate 143-I MDI curative (diphenylmethane diisocyanate)</td>
<td>2.1%</td>
</tr>
<tr>
<td><strong>AP</strong></td>
<td>86%</td>
</tr>
<tr>
<td>Coarse (200 micron)</td>
<td>43%</td>
</tr>
<tr>
<td>Fine (90 micron)</td>
<td>43%</td>
</tr>
<tr>
<td>Ingredient</td>
<td>% by Mass</td>
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</tr>
<tr>
<td>Coarse (200 micron)</td>
<td>35%</td>
</tr>
<tr>
<td>Fine (90 micron)</td>
<td>35%</td>
</tr>
<tr>
<td><strong>Aluminum</strong></td>
<td>16%</td>
</tr>
<tr>
<td>Al: ValleyMet H-15</td>
<td>16%</td>
</tr>
</tbody>
</table>

Table 3.2. Propellant ingredients and mass proportions for aluminized propellant
Figure 2.1. Change in slope from -2 to -1 at some critical point
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Figure 5.2. Uncovered Non-Al samples with experimental data trend line (-1.7231 slope) and error bars for the flux and ignition time
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Figure 6.3. Ignition time versus absorbed flux using absorptivity of 0.50 for the uncovered propellants tested with single theoretical -2 slope line.
REFERENCES


