Optimization of an Ammonium Nitrate Based Solid Rocket Propellant

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Abstract

The objective of this project was to design and optimize an ammonium nitrate based solid rocket propellant. This was done by measuring the energy output of multiple propellant formulations. Before any experiments were conducted, significant research and calculations took place to narrow down an optimal starting point for the chemical equation for the propellant. Theoretical combustion products were considered in balancing the chemical equation in order to make predictions for maximum enthalpy outputs. A high pressure bomb calorimeter was designed and built for the experiments. Varying propellant formulations were tested and compared to isolate the peak energy output while minimizing solid waste to ensure that all of the reactants were consumed during combustion. A final formulation was selected and can now being tested in a linear strand burner to analyze the precise propellant burn rate.

Acknowledgments

Special thanks go to David Oliphant for the help and advice throughout this project.

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Chapter 1

Introduction

1.1 Purpose of Research

The purpose of this research is to optimize an ammonium nitrate based solid rocket propellant with a goal of future use as a sub-orbital rocket propellant. An ideal rocket propellant burns all of the reactants very quickly and at high temperatures (1500 - 3500 Kelvin), releasing a lot of energy in a very short amount of time. In theory, the greatest energy output during combustion would provide peak performance.

Ammonium nitrate fuel burns at a less desirable, lower temperature, around 1600 K [1]. The burn rate is also much lower than the typical industry standard—ammonium perchlorate based propellant. The attractive part of an ammonium nitrate propellant is the higher volume of gasses produced during combustion than the typical industry standard. The more gas that can be heated up and accelerated out the nozzle, the more thrust is produced.

1.2 Rocket Basics

Rocket propulsion is a very simple concept: create thrust by sending pressurized gas through a flow constricting nozzle. Basically, the faster you can eject the most mass through the nozzle, the higher the thrust. Combustion provides the best way to create the gasses needed for thrust that is high enough to allow rockets to overcome earth's gravitational pull. [15]

High performance rockets use a converging-diverging nozzle. The definition of a nozzle is a device designed to control the direction or characteristics of a fluid flow (especially to increase velocity) as

it exits (or enters) an enclosed chamber or pipe [2]. A converging diverging nozzle is a special nozzle that accelerates the combustion gas after the gas has passed thought the throat of the nozzle.
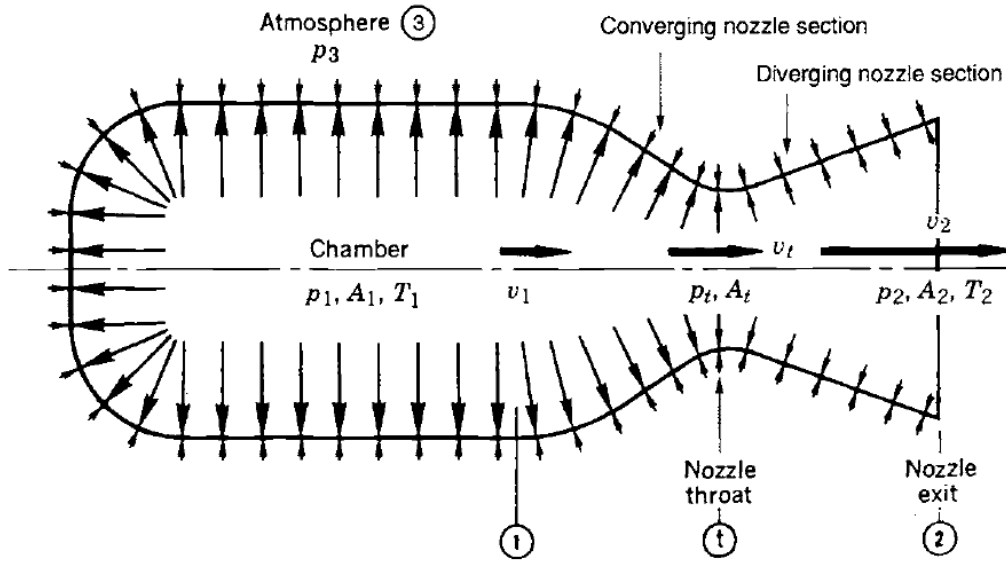
Figure 1-1 Converging - Diverging Nozzle
Chamber pressure and temperature is p_1 and T_1. Area of the throat and velocity at the throat is A_t and v_2. Exit parameters are signified by the subscript 2. Atmospheric variables are denoted by the subscript 3. [12]

As the nozzle cross sectional area increases past the throat, the gas will accelerate as it is allowed to expand with the wall of the nozzle. For choked flow of gasses, at the throat of the nozzle, the gas will always be traveling the speed of sound, or Mach 1. As the combustion gasses are allowed to expand with the diverging part to the nozzle, the gasses can reach velocities of Mach 3 or more, depending on combustion chamber pressure, temperature, atmospheric pressure, nozzle expansion ratio, among a myriad of other factors.

1.3 Nozzle Theory Equations
The initial basic design of a nozzle will be based on how fast the combustion gas can exit the nozzle and what the right size of throat and exit area the nozzle needs to have to produce that exit velocity. Exit velocity, Mach number, and nozzle dimensions are calculated with the following set of equations:

$$v_2 = \sqrt{\frac{2k}{k-1} RT_1 \left[1 - \frac{p_2}{p_1}^{\left[\frac{k-1}{k}\right]} \right]} \tag{1}$$

$$M_2 = \sqrt{\left(\sqrt[\frac{-k}{k-1}]{\frac{p_3}{p_1}} - 1\right)\frac{2}{k-1}} \tag{2}$$

$$A_t = \frac{\dot{m}}{p_1}\sqrt{\frac{RT_1}{k\left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}}} \tag{3}$$

$$\frac{A_2}{A_t} = \frac{1}{M_2}\left(\frac{1+\frac{k-1}{2}M_2{}^2}{\frac{k+1}{2}}\right)^{\frac{k+1}{2(k-1)}} \tag{4}$$

Where k is the specific heat of the combustion gasses, R is the ideal gas constant , M_2 is the exit Mach number and, $\dot{m}$ is the mass flow rate of the combustion gas through the nozzle. Combustion gas properties and pressures are the key factors in chemical rocket propulsion. Before any of these equations are useful, a chemical propellant mixture must be chosen in order to determine these basic variables.

The approach taken with this research was to find an ammonium nitrate based propellant that produces the highest possible energy release upon combustion. Once found, the propellant can be further examined to discover the specific heat ratio of the combustion gas, burn temperature, and the burn rate needed to calculate the mass flow rate.

1.4 Relevance of research
High energy ammonium nitrate propellants are attractive for cheap sounding rockets. Sounding rockets are rockets designed to reach sub orbital elliptical trajectories carrying scientific equipment. Sounding rockets provide access to areas in the atmosphere inaccessible by weather balloons or too low for satellites. These rockets are made available to researchers at low cost. Sounding Rockets are commonly used for research in X-Ray astronomy, microgravity and aeronomy [3].

Sounding rockets are generally solid fueled which are less complicated and offers short lead times than their liquid fuelled counterparts. One style of sounding rocket, liquid or solid, is not better than the other. It all depends on the mission requirements. Some missions are more suited for the lower acceleration typical of an ammonium nitrate based propellant. This propellant is cheap, safe to handle, plentiful, and easy to manufacture.

Chapter 2

Propellant Background

2.1 solid propellant basics

Solid rocket propellants consist of a fuel, oxidizer and binder. The fuel can be anything that releases a lot of energy when combined with an oxidizer in a combustion reaction. Over the years of solid rocket propellant development, metals were found to offer the highest energy for a fuel.

The most widely used solid propellant is an aluminum powder and ammonium perchlorate mixture. There are others that are higher performance but given manufacturability, safely and a proven track record, the Al/AP mixture is the most popular.

2.2 Ammonium Nitrate Based Propellant

The ammonium nitrate based fuel is an under developed solid propellant [4]. Ammonium nitrate has a number of qualities that make it an appealing rocket propellant oxidizer. It is used as an agricultural fertilizer and, therefore, is readily available at low cost. It does not burn on its own, and has a low sensitivity to friction. Ammonium nitrate is safe to handle and the combustion products are nontoxic. When ammonium nitrate it heated it will decompose solely into gaseous products. This contributes to low molecular weight combustions products, which then leads to a higher specific impulse [4]. Specific impulse, or Isp, is the basic parameter used to calculate the performance of a rocket. The higher the Isp the more efficient the rocket.

The high gas generation of an ammonium nitrate oxidizer propellant is useful in many applications. The most common use is in air bags. Low combustion temperatures coupled with extremely high amounts of gas generated offer the ideal scenario for safely deploying an air bag with the least amount of explosives involved.

Ammonium nitrate propellants naturally have a slower burn rate because of the lower burn temperature. A slower burning rocket propellant is useful for long burn time applications, which can provide greater dynamic stability for a long distance tactical missile, for instance. Tactical missiles also benefit from the faintly visible plume of the transparent or smokeless ammonium nitrate based propellants [5].

2.2.1 The Physics and chemistry of Ammonium Nitrate

Ammonium nitrate has some unique properties which make it useful in wide range of applications. Ammonium nitrate does not burn by itself. Under ambient conditions it is chemically stable and can safely be stored by itself in large amounts without fear of spontaneous ignition. Ammonium nitrate

is very hygroscopic. Actions need to be taken to store the chemical in a dry location, or at least keep it in a sealed container and not left out in the open.

In a combustion reaction, ammonium nitrate will decompose in both an exothermic and endothermic reaction simultaneously. This neat feature is what causes the biggest challenges for use as the oxidizer in a rocket propellant, but is also what makes this a great rocket propellant. The two reactions are broken down as follows:

Exothermic
When ammonium nitrate (NH_4NO_3) is heated to the range of $200°F - 250°F$, it will decompose and release energy resulting in gaseous nitrous oxide and water vapor.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \tag{5}$$

This exothermic reaction will produce about $-36\ kJ/mol$. [4]

Endothermic
Simultaneous to the reaction just mentioned, a dissociating reaction occurs where the ammonium nitrate breaks down to ammonia and nitric acid.

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 \tag{6}$$

This endothermic reaction will consume about $186\ kJ/mol$. [4]

Without sustained heat supplied to the reactions, the endothermic reaction will overpower and snuff out the combustion. This is also a contributing factor to the slower burn rate associated with ammonium nitrate.

Aluminum burns at approximately $1400°F$ and, when mixed with ammonium nitrate in the proper proportions, offers sufficient heat to sustain the reactions.

Phase Stabilized Ammonium Nitrate
There is one inconvenient drawback to using ammonium nitrate as an oxidizer. Ammonium nitrate will undergo a five phase change at different temperatures [4]. The volume of the ammonium nitrate compound will increase with elevated temperatures during phase changes. Volumes can increase up to 4%[4] as seen in figure 2-1. At about 30 and 100 degrees Fahrenheit ammonium nitrate will experience a phase change and increase in volume. This can be very problematic if storage and transportation would expose the propellant to these temperatures. There is little to worry about if everything happens within these temperatures.

Phase stabilization of ammonium nitrate is a well-researched topic. There is lots of information on line. In short, combinations of potassium nitrate or zinc mixed with ammonium nitrate are very affective for stabilizing ammonium nitrate [6]. Given the time scope of this project, phase stabilization was not pursued. When this propellant is actually tested in a rocket engine, it should be phase stabilized first and then analyzed for burn rates etc.
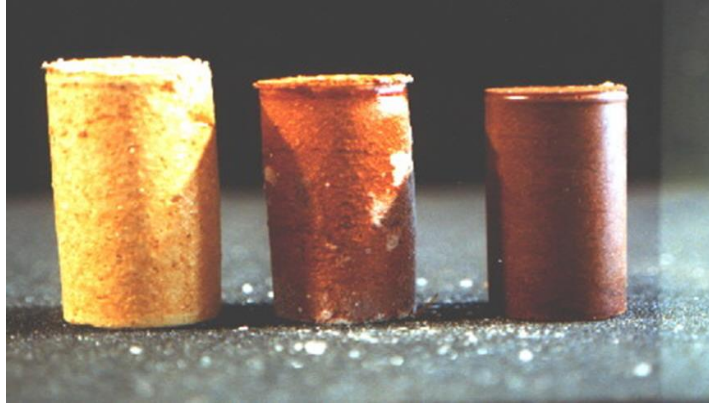
Figure 2-1: Phase Change of Ammonium Nitrate
The samples were heated to 120 °F.
The middle cylinder shows what happens to a composite propellant with un-stabilized ammonium nitrate. The cylinder on the right is phase stabilized with a formula using 3% zinc oxide. It is its original size after a month of temperature cycling. The cylinder on the left was "stabilized" with Urea which obviously was less than successful [6].

2.3 Aluminum

Aluminum powder is the fuel in the propellant mixture. A metalized fuel is needed to supply the intense heat required to sustain combustion with ammonium nitrate. Other metals, such as magnesium, will work well, however, aluminum was chosen because of the low cost and ease of access [13].

There are many different types of aluminum powders and they all affect the propellant performance. It does not matter which one is used as long as fuel batches are consistent. For this research German black 2 micron aluminum powder was used. See appendix for chemical suppliers.

2.4 Sulfur

Sulfur is a vital ingredient to the solid propellant. In combustion reactions, sulfur acts as a combustion stabilizer reduces the ignition temperature of the propellant. Sulfur contributes to a more vigorous and complete consumption of the propellant compound.

Multiple recipe combinations were tried in which the sulfur percentage varied. The propellant samples would not sustain ignition without even a very small amount of sulfur. The suitable sulfur percentage turned out to be 0.66% by mass. This percentage was determined by evaluating the combustion efficiency and ease of ignition.

2.5 Binder

A binder is required to ensure the tensile strength of the propellant fuel grain. Rocket propellant requires a predictable stable burn in order for the engine to perform properly. A propellant without a suitable tensile strength can deform and even break apart under the immense pressures (up to

1000 PSI) exerted on the fuel cell during the rocket engine burn. This will almost certainly result in a catastrophic failure of the engine.

Propellant binders are generally a glue of some sort. The binder most popular, industry wide, is an HTBP Epoxy [16]. Epoxy is very strong, doesn't inhibit the combustion, and cures fast. To try something new, and continue with Richard Nakka's research, a neoprene based binder was used.

DAP brand contact cement was used in these experiments. This cement consisted of 60% toluene (C_7H_8), 20% petroleum distillate (C_6H_6) and 20% methyl ethyl ketone or butanone (C_4H_8O). These chemicals were accounted for by mass percent in the initial design of the chemical formula. During the curing process of the contact cement, the compound loses mass. It was determined—by consulting some chemistry professors that after the curing process, the remaining binder compound was benzene (C_6H_6). After this research was conducted, there was concern that the remaining compound would not be benzene. This was not deemed a very critical mistake in the fact that it is only hydrocarbons and will not significantly affect the combustion of the propellant. After all, the compound C_6H_6 was only used to determine a starting point for the chemical equation. Possible chemical formulations and combustion produces are discussed further in section 3.2.

Chapter 3

The Bomb Calorimeter

3.1 bomb calorimeter

In order to determine an optimum propellant mixture, the energy output needed to be measured. This is best done with a bomb calorimeter.   A bomb calorimeter is a device that allows the energy of a substance to be measured by way of combustion. Figure 3-1 is a basic bomb calorimeter.
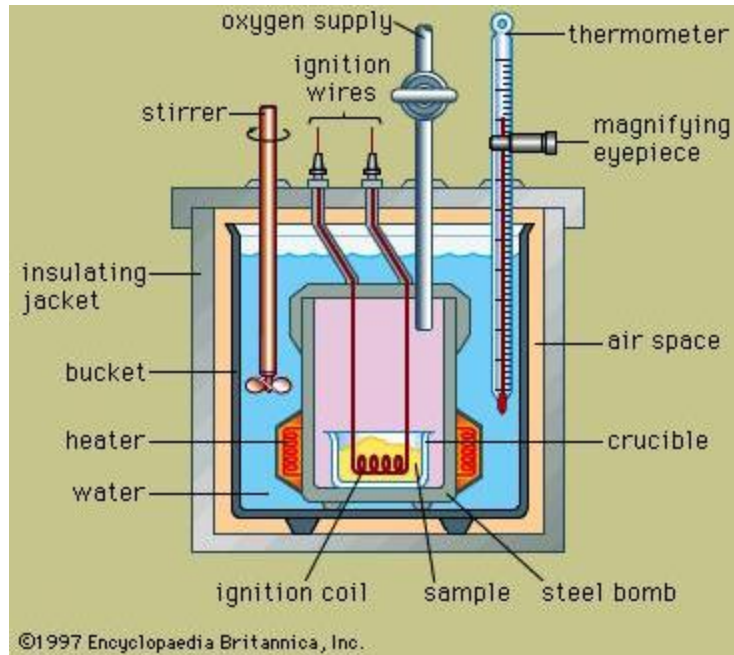
Figure 3-1: Bomb Calorimeter [5]
This is an example of a typical bomb calorimeter. The one built for this project differs in that there is to oxygen supply and the insulating jacket and bucket are the same.

The sample to be tested is placed in the sample cup. The bomb is then purged with enough oxygen for at least stoichiometric conditions. The vessel is submerged in water. Electric ignition leads are connected to the vessel and the sample is then ignited. The energy released from the combustion heats up the bomb and water. The measured temperature change is what is used to calculate the energy released. This is done by applying the first law of thermodynamics.

$$Q + W = \Delta U + \Delta KE + \Delta PE \qquad (7)$$

For the case of testing rocket propellant, there is no need to purge the bomb with oxygen. Solid rocket propellants have their own oxidizer, in this case, ammonium nitrate.

Bomb vessels come in different variations depending on the application. The vessel used in this research is the Parr Instruments 1104 High Strength Bomb, see figure 3-3. This bomb is intended for testing actual high explosives and is rated for a max pressure of 10,000 PSI. Standard working pressure, however, should be kept to about 3000 PSI.

3.2 Theoretical chemical formula

In order to begin the search for the optimal rocket propellant chemical formula, a chemical equation needed to be balanced using the components decided on. This was to be a stoichiometric balance. Since the products were not entirely known, an excel sheet was created to try different balances given probable combustion products. Several balanced equations resulted.

The equation narrowing down process was to use the parabolic curve fit method. The formulas were varied by changing one chemical a certain percentage while keeping the others stationary. Doing this would provide a 2 dimens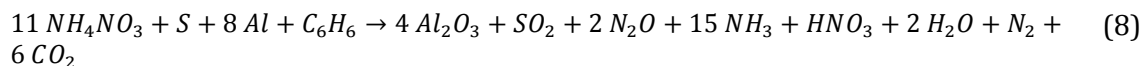ional plot of energy data points that a parabola could possibly fit. Once an apex is found, another chemical would be varied providing a third axis of data where a 3 dimensional parabola could be fit. This would theoretically find the highest energy possible given the chemical combinations. As data was taken, this approach was altered as explained in chapter 7.

Table 3-1: Excel sheet used to find possible balanced Equations.

Blue is the reactance and gray is the products. The red cells are molecules with a fixed mole amount. The yellow cells are the molecules whose moles could vary in order to find the balanced equations.

	NH4NO3	S	Al	C6H6	Al2O3	SO2	N2O	NH3	HNO3	H2	H2O	N2	CO2		
	A	B	C (even#)	D	E	F	G	H	I	M	J	N	K		
Moles	11	1	8	1	4	1	2	15	1	0	2	1	6		
Molar Mass:	80.053	32.06	26.98154	78.048											
	880.583	32.06	215.8523	78.048	1206.543										
% Composition:	0.72984	0.026572	0.178901	0.064687											
N:	22						4	15	1			2		0	N
O:	33				12	2	2		3		2		12	0	O
H:	44			6				45	1	0	4			0	H
C:				6									6	0	C
Al:			8		8									0	Al
S:		1				1								0	S

	NH4NO3	S	Al	Binder	Total Grams
Recipe for 10 grams	7.298395	0.265718	1.789014	3.2343638	12.58749102

It was known—from researching other work done by Richard Nakka—that the higher the aluminum percentage, the better. One balance was chosen for testing because only one showed an acceptably high enough aluminum percentage. The balanced equation was

$$11\ NH_4NO_3 + S + 8\ Al + C_6H_6 \rightarrow 4\ Al_2O_3 + SO_2 + 2\ N_2O + 15\ NH_3 + HNO_3 + 2\ H_2O + N_2 + 6\ CO_2 \qquad (8)$$

This formula results in percent masses in table 3-2.

Table: 3-2 Percent mass formula

One of the percent mass formulations tested that was determined by balancing the chemical equation.

72.98 %	NH_4NO_3
17.89 %	Al
2.66 %	S
6.47 %	C_6H_6

3.3 Safety calculations

Before any experiments were conducted, thorough calculations were completed to estimate the max pressure the vessel would experience during combustion of the propellants. A conservative approach was taken to ensure any uncertainties would not decrease the factor of safety. Some of these conservative assumptions were:

All the combustion product masses were assumed to be in gas form.

The bomb calorimeter is a perfect closed system.

The goal for a factor of safety would be for the calculated pressures to be close to one order of magnitude bellow the max rated pressure of the bomb.

To estimate the change in pressure a formula was needed for pressure as a function of energy put in the system. This was done by combining the first law of thermodynamics in the form of

$$Q = mc\Delta T \tag{9}$$

And, a differentiation of the ideal gas equation with respect to temperature, written as,

$$dp = \frac{nR}{V} dT \tag{10}$$

Solving for ΔT and substituting for dT, the combined equations form

$$P(Q) = \frac{nR}{Vmc} Q \tag{11}$$

The heat Q can be re-written as just the change in enthalpy ΔH because there is no work done on the system because of the constant volume of the bomb. Assuming all the mass turns into gas and using the specific universal gas constant $R_{specific}$. The equation can be re-written as

$$P(Q) = \frac{R_{specific}}{Vc_p} \Delta H \tag{12}$$

With this equation, a max pressure was able to be approximated. Furthermore, plots of pressure vs. mass of propellant were made after calculating a rough heat of reaction (ΔH) for the theoretical

propellant chemical equation. This was convenient for understanding the limit of propellant mass that could be safely ignited in the bomb. It turned out—to our benefit—that not enough propellant could be held in the sample cup to exceed the working pressure of the bomb, which is 3000 PSI.
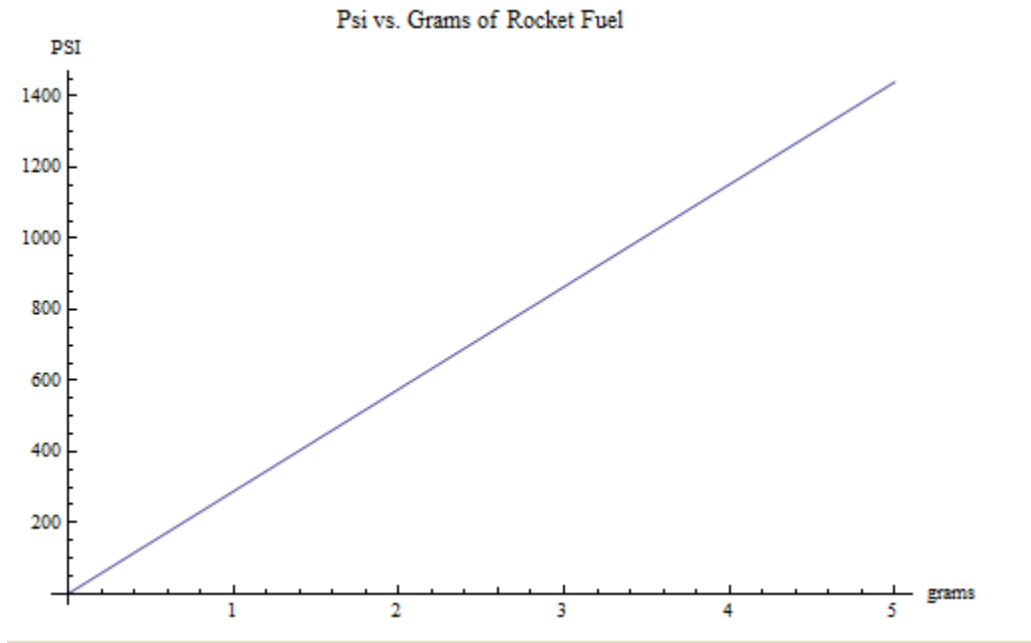

Figure 3-2: PSI vs grams of propellant
This figure shows a plot of the projected pressure in the bomb vessel given how much propellant is combusted. 5 grams is the max amount of propellant that could be put in sample cup.

From these calculations, it was concluded that the planned experiments would not put any people or hardware in danger under nominal test procedure operations.

3.4 calibration of the bomb calorimeter

There is a correction factor that must be accounted for with the bomb calorimeter. Since the insulating jacket is not a perfect insulator, there are minor heat losses that still need to be accounted for. This value is specific to a device and can be found by measuring the energy output of a known sample. The correction factor, β is the ratio of actual energy over measured energy

$$\beta = \frac{Q_{actual}}{Q_{measured}} \tag{13}$$

This correction factor is known as the calibration constant for the bomb calorimeter.

Generally, the fuel used to calibrate a bomb calorimeter is benzoic acid, because of its well-known heat of combustion and clean burning. Using benzoic acid to calibrate the bomb used for this research was not the best plan. The added oxygen in the system for calibration would cause an inconsistency of the specific heat of the system between calibration and tests. As mentioned before, supplied oxygen is not needed for testing the combustion of rocket propellant because the

propellant has its own oxidizer. It was assumed that this discrepancy was significant enough resulting in the need for an alternative calibration constant. In retrospect, considering the uncertainties found in the testing, this oxygen discrepancy probably would not have been significant enough to change the overall results. Regardless, a smokeless, rifle ammunition reloading gun powder was selected for the calibration standard. Reloading powders are very consistent in their combustion. They need to be consistent in order for rifles to operate safely and reliably. This combination is ideal for a calibration standard. The rifle powder Hodgdon 414 was selected. The company that makes the powder was kind enough to share the thermodynamic properties of the rifle powder. See table 6-1for H414 properties.

Hodgdon 414 was used as the calibration standard with great success. Many calibration tests were conducted to find the calibration constant β. Ideally, the more test data points there are, the more accurate the calibration will be. Since the kinks of the bomb calibration set up were being worked out as the calibration was being conducted, only ten tests were deemed acceptable. Nevertheless, a value for β was found to be 1.67 ± 0.01. Details of test data calculations are in chapter 6. Further detail on how the bomb calorimeter is calibrated is outlined in chapter 4.

3.5 Calculating the energy output

For a closed system the first law of thermodynamics can be written as [10]

$$Q + W = \Delta U + \Delta KE + \Delta PE \tag{14}$$

For this case, the potential and kinetic terms are negligible. The vessel does not change in volume so the work done is zero. The equation reduces to

$$Q_v = \Delta U \tag{15}$$

Also note that for ideal gasses the equation can be written as

$$Q_v = \Delta U = \Delta H - m_{gas} R \Delta T \tag{16}$$

The energy released can be written as the change in enthalpy of the system. This it rewritten as

$$\Delta H = \beta (m_w c_w + m_{ss} c_{ss} + m_{gas} R) \Delta T \tag{17}$$

Where β is the calibration constant. The masses, m_w and m_{ss}, are of the water and the stainless steel bomb. The specific heats of the water and the stainless steel are the c_w and c_{ss}. The term $-m_{gas} R$ relates the internal energy ΔU to the change in enthalpy ΔH. This term is negligible considering the mass of the combustion gasses are so small compared to the mass of the water and stainless steel bomb.

The calibration factor takes into account the specific heat and mass of other small part such as the mixing probe, combusted product gas etc. It is very important that everything stays consistent between calibration and running experiments for the calibration factor to be reliable.

3.6 Building the bomb calorimeter

The Chemistry department's bomb calorimeter was unavailable so action needed to be taken to either build or buy one. Unfortunately, both options proved far too costly. Luckily, several bomb vessels were found on eBay for a great price. Four vessels were purchased for about $500. Two of which were good enough to use. The others were used as parts. A single brand new vessel would cost about $7,000. These vessels were manufactured by Parr Instruments[6].

Figure 3-3: 1104 High Strength Bomb
Manufactured by Parr Instruments

A rebuild kit was purchased from Parr and one of the vessels was refurbished. A single refurbish kit costs $150. Instruction and diagrams of the vessel can be found at the Parr instruments web page [8]

A simple two gallon cooler was used as the insulating container. Insulation was added to the lid. A circulation motor was fitted to the top of the lid. This motor was wired to an adjustable amperage power source so the motor speed could be controlled. Water circulation is needed to eliminate any hot or cold spots in the water resulting in a faulty temperature reading. The threads on the lid and the jug were removed so the lid could come off without any turning.
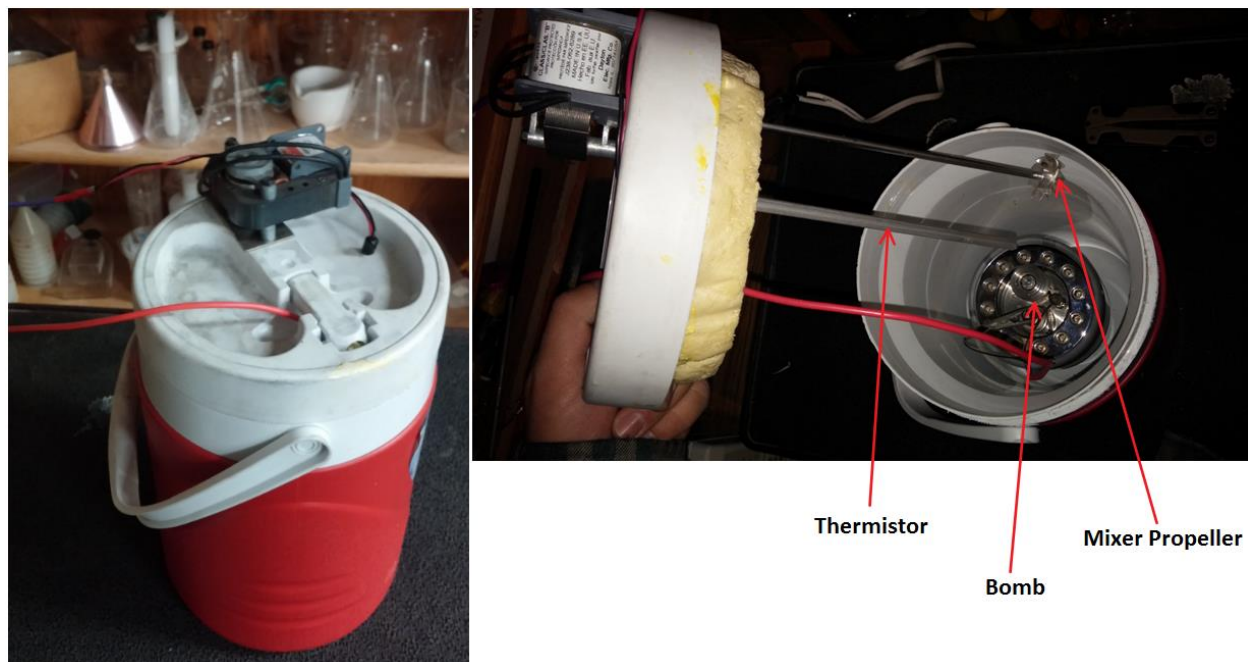
Figure 3-4: Student designed Bomb Calorimeter
Made from a two gallon cooler

3.7 Data collection.

Data collection was done through a simple LabVIEW program. Data was read in through a DAQ at 0.2 Hz. A high sample rate is not necessary because the temperature changes happened fairly slowly. The important part of the data is the beginning temperature and ending temperature values. The difference of these values is what is used to calculate the overall energy released.

Built into the LabVIEW program was a heat dissipation curve fit to the collected data, courtesy of David Oliphant. This was done in an effort to sharpen the uncertainty in the initial and final temperature measurements. The best resolution that was gleaned from using the DAQ/LabVIEW system was ±0.022 degrees F. For details on the LabVIEW program, see appendix.

3.7.1 Measuring the temperature change

A Thermocouple was used to measure the temperature change. It was in inserted in through the top of the lid. The Thermocouple was not purchased but was borrowed from one of the physics labs. A thermocouple reports a temperature by the changing resistance from the thermocouple being in an environment. In order for this temperature data to be collected, a change in resistance converted into a voltage needs to be reported by the thermocouple. Figure 3-6 is the wiring diagram for thermocouple.
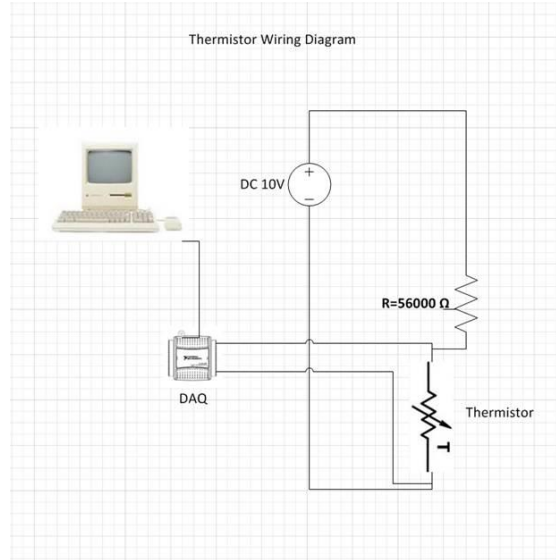
Figure 3-5: Thermistor Wiring Diagram
The Voltage settings for the power supply will vary with the calibrations and will directly affect the precision of the temperature measurements. For this research, V_o was set to 23.6 Volts.

A thermocouple needs to be calibrated. This is done by placing the thermocouple in a beaker of water with a known cold temperature. The water is then heated up on a hot plate. Measurements of resistance of the thermocouple and temperatures are taken as the water is heated up. There should be twenty or more measurements. This data is then plotted with each other and made to fit the curve using the Steinhart-Hart equation to get temperature as a function of resistance.

$$\frac{1}{T} = A + B \ln(R) \tag{18}$$

Where T is the temperature and R is the resistance. The variables A and B are the Steinhart-Hart coefficients. Figure 3-6 is a plot of the thermistor calibration used in for this research.
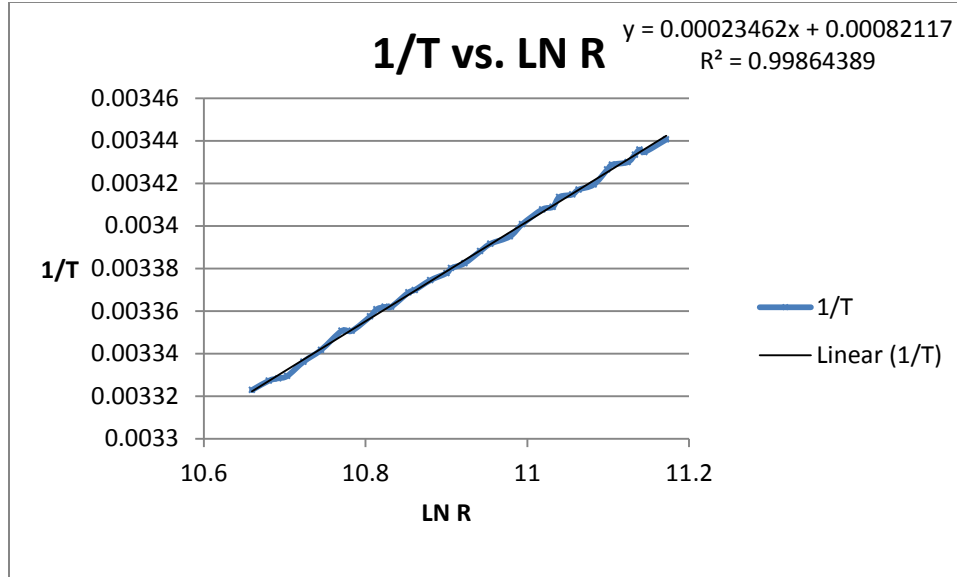
Figure 3-6 Inverse Temperature vs. the natural Log of Resistance

This fitted curve gives the values of a and b which are now specific to this thermocouple at this time. This calibration needs to occur periodically. With the case of the bomb calorimeter, an exact temperature value is not of high importance. The temperature <u>change</u> is what is needed. This allows for a little flexibility in the accuracy of the thermocouple. Throughout the experiments conducted, the assumption was made that the slope of the thermocouple curve stayed the same, thus resulting in consistent temperature change between experiments and not necessarily accurate individual temperature values. Again this was an assumption. The thermocouple was only calibrated twice during the entire research project.

The data is useless unless it can be in the form of temperature vs. voltage. Combining the Steinhart-Hart equation with the voltage balance equation for the thermostat circuit, we have temperature vs. voltage in the form of:

$$T = \frac{1}{A + B \ln[R_1 \left(\frac{-V_0}{V - V_0} - 1\right)]} \tag{19}$$

Where V_0 is the power supply voltage and R_1 is the $56000\,\Omega$ resistor in the circuit and V is the measured voltage output by the DAQ.

Chapter 4

Propellant Mixing

4.1 Ammonium Nitrate Preparation

Ammonium nitrate generally comes in the form of small spheres. These will need to be ground up before it can be used for propellant mixing. The general rule of thumb is the smaller the particle size the more homogeneous the propellant mixture and the better and more complete the combustion.

An electric coffee grinder was used to grind up the ammonium nitrate into a fine powder. Bear in mind that ammonium nitrate is very hygroscopic. Once the ammonium nitrate has been ground up, it will absorb moisture in the air faster than in the larger granular form. Once the ammonium nitrate has been ground, place it immediately in an airtight container and set aside until it is ready to be opened for weighing and mixing. It is crucial that the ammonium nitrate be exposed to the moisture in the air as little as possible.

4.2 Weighing and mixing the chemicals

Each chemical needs its own dish or container to weigh the samples in. It is important that these containers are not cross-contaminated amongst each other. Before weighing a sample, the container should be filled with the chemical and dumped back. By doing this, the scale will then be zeroed with a dish that has been "dirtied", resulting in a more accurate measurement of what will be poured into the propellant mixture.

Figure4.1: Individual chemicals stored properly in jars
From left to right: Ground ammonium nitrate, aluminum powder, sulfur.

Once the individual chemicals have been weighed out separately, combine them all in a mixing bowl. Generally when working with pyrotechnics, stainless steel or polyethylene products are best used to guard against static hazards. Spend time to mix the chemical thoroughly.

Once the chemicals have been mixed, they will then need to be added to the binder. The best way to do this is to have another clean mixing bowl zeroed on the scale and the contact cement binder poured into that new mixing bowl. Once the binder has been measured out, the dry chemical is then poured in with the binder. When mixed correctly, the consistency of the binder with the dry chemicals will be similar to that of playdough.

This final mixture now needs to go through a curing process. The way the propellant is cured is different depending on the end use either being for a small test or made in large quantities to be used in rocket engines. For the purpose of this research, propellant was only made in small quantities. The curing process specific to small quantities is to spread the propellant evenly across wax paper. Doing this speeds the curing process along at a faster pace. The propellant should be left to cure for at least twelve hours or until it is dry.

4.3 preparing the test samples

Once the propellant is cured, it gets broken up into small bits manually or through a coffee grinder dedicated only to the use of grinding up propellant. The propellant samples then get made into small donut shaped disks as seen in figure 5-4 these disks are made by compressing the propellant in a mold under a hydraulic press. This is a very technical step and is an acquired skill through a combination of practice and trial and error. This process took many trials to result in a working solution. A completed sample disk should weigh between 1.0 – 4.0 grams.

As seen in figure 5-4, the sample disk can now be thread onto the ignition wire coil and be wired to the ignition probes on the bomb assembly. Further details preparing the ignition wire coil is in chapter 5 step three. The reason the disk is doughnut shaped is to help with ignition. Having the ignition coil go through the center hole allows for even energy transfer to the sample.   Ammonium nitrate propellants are harder to ignite than most solid rocket propellant, so the more concentrated the heat source the easier the ignition.   The ignition wire is coiled up to provide the heat concentration, much like a light bulb. Multiple wire ignition configurations were tried and this was by far the best.

Chapter 5

Test Procedures

5.1 Equipment

The experiment set up is simple, see figure 5-1. For the test, the calorimeter will need to be in the fume hood with the fan on. The experiments took place in the chemistry lab shared by the Geology and Physics department.
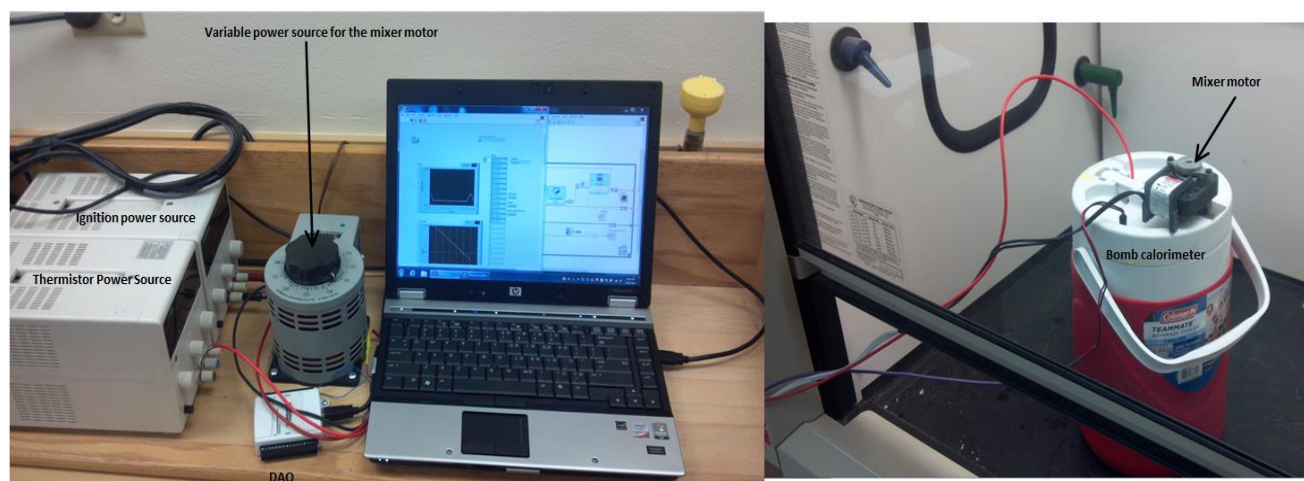

Figure 5-1 Equipment Set Up

Table 5-1
Test Equipment and tool list

| ITEM	Details
Ignition power source	Amperage set to about 8. Volts set to about 5
Thermistor power source	Voltage set to 23.6
Lap top and DAQ	Needed to collect data using labVIEW
Variable power source for the mixing motor	Generally set to 35%
Bomb calorimeter	Insulated container and SS vessel
Beaker stand	See figure 5-4
Scale	For weighing the water see **step 6**
Tungsten wire	Ignition wire
Plyers and wire cutters	For making the ignition wire
DI water	For filling the insulated container
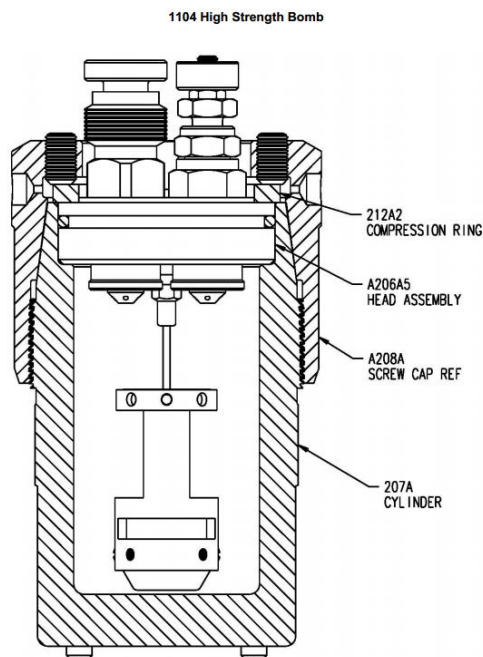
Figure 5-2 1104 High Strength Bomb
This is the 1104 high strength bomb manufactured by Parr instruments. This diagram varies slightly from the one used for this project. The only difference is the sample holder.

5.2 Detailed steps to operating the bomb calorimeter

These steps are for both calibration and actual sample analysis. The bomb calorimeter is a precision device that requires attention to detail and an eye for safety and potential problems. The system is not perfect which results in a lot of trial and error. The key to success is to have a clean area—clean as you go—and to be meticulous with being consistent in all the operational steps.

Step 1. Clean the vessel

- Clean inside the bomb vessel. Generally wire brushing is required to remove combustion deposits from previous tests. Use water and/or rubbing alcohol to clean the surfaces. Remember to clean the sample holder cup. Blow through the ports with compressed air.
- Verify everything is in working order.
- For convenience, mount the head assembly in the clamp stand as seen in figure 5-4.

Step 2 Weight the sample

- Weigh the sample and record it. For calibration, use the Hodgeon 414 smokeless powder. For technical information on H414 [9] see table 6-1. It does not matter what the sample weight is for the test as long as that weight is used in the post test calculations. Generally, about 2 grams of H414 was used in the calibration tests.

Figure 5-3 Hodgdon H414 Rifle Powder

- Insert the weighed sample in the clean holder cup.

Step 3 Attach the ignition wire

- Attach the ignition wire. This is an acquired skill. Use the spool of tungsten wire as the ignition wire. This is used because tungsten wire can stay hotter longer without breaking unlike the nickel wire usually used as ignition wire for bomb calorimeters. Cut about six inches off the spool. In the middle of the wire, wrap the wire several times around a 1/16 inch diameter rod, creating a coil. Make sure the individual coils do not touch. Doing this provides a heat concentration which is ideal for ignition. The wire must be attached from the ground lead to the insulated positive lead. The wire must come in contact with the sample. See the Parr oxygen bomb user's manual on their web site for further instruction[7].

Figure 5-4 Head assembly in stand
Head assembly with propellant sample wired to ignition leads

Step 4 Insert Head Assembly
- Make sure the black seal is not damaged.
- Carefully insert the cap assembly into the vessel, rough movements can dislodge the sample or the ignition wire.
- Make sure the compression ring is in place on top of the head assembly.

Compression Ring

Figure 5-5: Head Assembly in Stand 2
Also pictures are the cylinder vessel, and compression ring

Step 5 Screw on Cap
- With finesse, screw on the cap hand tight and hand tighten the Allen screws in a star pattern.
- Make sure the vessel is not bumped or in the way for possible movement.

Step 6 Fill the Cooler with DI water
- Fill the cooler with 2.0295 kg of DI water; put the cooler in the fume hood. The only reason this number was used is because it was convenient and was easier to be consistent.
- While wearing rubber gloves, place the vessel in the DI water. The water level should cover the entire vessel and pass-through ports on the head assembly.

Step 7 Connect ignition Leads
- Connect the positive line to the insulated lead and the negative wire to anywhere on the vessel, see figure 5-6.
- **** Warning**** be sure the ignition source is off prior to hooking up the leads!
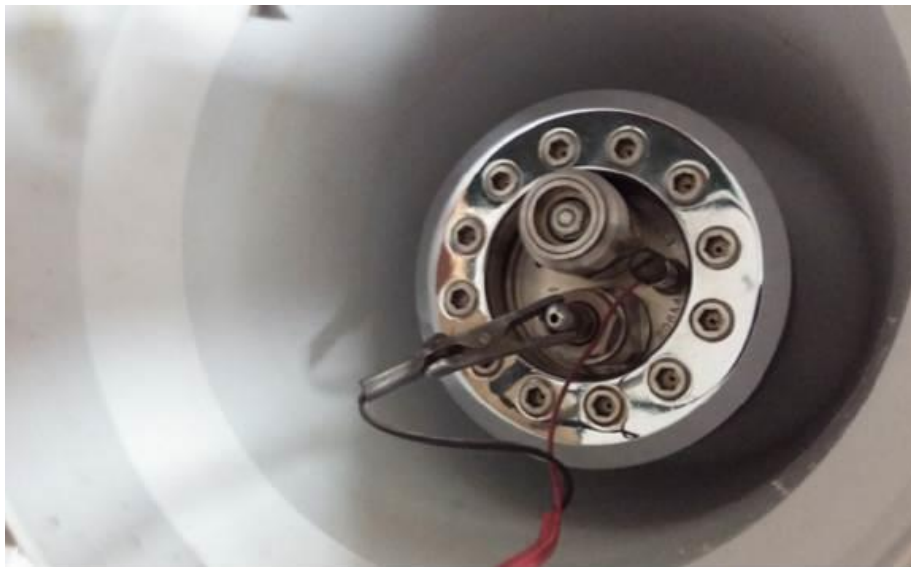

Figure 5-6: Ignition Conection

Step 8 Place Lid on Cooler
- Place the lid on the cooler. Make sure the mixing propeller has room to spin freely.
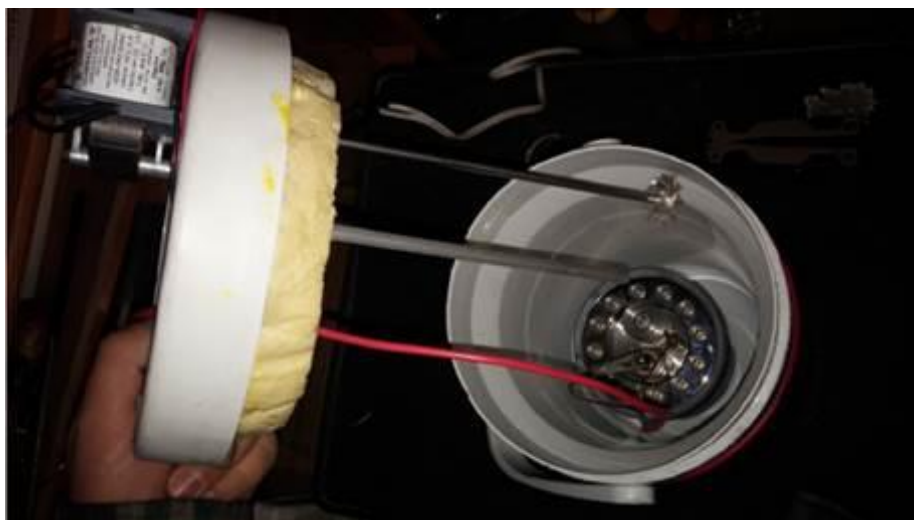
Figure 5-7: Lid Assembly

Figure 5-8: Bomb Calorimter in the Fume Hood
State of the bomb calorimeter during a test

Step 9 Run Test

- Turn on the mixer power source, set to 35%. Verify the mixing shaft is spinning and not knocking against the vessel.
- Turn on the thermistor power source, set the voltage for the calibration. For this project the voltage was set to 23.6 Volts.
- Start temperature data collection in LABVIEW.
- With the ignition power source pre-set to approximately 8 A, turn on the power supply to ignite the sample, combustion should occur and the temperature should rise immediately. Be sure to test different amp settings for the ignition wire until a comfortable setting is determined.
- Immediately after ignition is confirmed, turn off ignition power. Doing this ensures electrical energy is not being added to the system.
- Leave the program running until the temperature is no longer climbing. This generally took about 10 minutes.
- End LABVIEW program, was the program used for this project, the data was saved automatically. In any case, verify the data was collected and saved
- Record the temperature difference. Or any anomalies that might have occurred

5.3 Post Test Procedures

- Turn off all power sources
- Open the insulated container and disconnect the ignition leads.
- Remove the vessel and dry off completely before opening.
- Open vessel and record finding of combustion remains.
- Clean inside the vessel. Blow out any small orifices with compressed air.
- Clean area.

5.4 Procedure notes

It is very important to be consistent with cleaning the bomb, filling the water and walking through steps in the same way every time. Consistency is a must in order for the calibration constant, β to accurately reflect the energy output of the sample.

Keep track of the temperature measurements and uncertainties in a note book. Once temperatures are taken, calculate the energy output kJ/kg of fuel. Take particular note to the combustion results of the material. Never assume the test will go as planned.

Chapter 6

Calculations

6.1 Calibration Data

Before the bomb calorimeter could be used for any unknown energy measurements, the calibration constant β needed to be found. A total of ten tests were completed using the Hodgon H414 rifle powder as the calibration standard.

Table 6-1
List of constants and uncertainties used in the calculations

V (m^3)	0.000240	±	0.0000001	Volume of bomb
R (kJ/K mol)	0.008315	±	-	Gas constant
mw (kg)	2.0847	±	0.0001	Mass of water
mf (kg)	0.003174	±	0.000001	Mass of propellant sample
mb (kg)	5.21	±	0.001	Mass of bomb
cw (J/kg K)	4182.0	±	-	Specific heat of water
cs (J/kg K)	502.0	±	-	Specific heat of Stainless steel
ΔH 414	-3.5797	±	0.0001	Energy density of the rifle powder

The uncertainties in the measurements were calculated and are displayed in Table 6-2. The average of the β values was calculated to be 1.07. The uncertainty was found by dividing the standard deviation by the square root of the data set.

$$\delta = \frac{\sigma}{\sqrt{10}} \tag{20}$$

This value β represents losses in the system. Bomb calorimeters will general have a calibration constant of a little over 1.0. The constant derived in this project right in line with what we would expect, not too bad considering it is made from a cooler.

Table 6-2 Calibration Constant

β value data from ten tests and uncertainties. Equations 17 and 13 were used to calculate the calibration constant.

β
1.081
1.071
1.061
1.059
1.087
1.067
1.081
1.055
1.085
1.075

Average β	1.072
Standard dev.	0.011
uncertainty	0.004
Percent Uncertainty	1.1%

6.2 Experimental Data and Calculations

Many tests were conducted with different combinations of the propellant recipe. This paper will not cover all the different formulas. Please reference the thesis written by David Newey for details on the multiple recipes tried.

After several tests were conducted with varying recipes, a trend was noticed. The higher energy outputs and best combustion was constant with the increase of aluminum percentage and decrease of sulfur percentage. There was a limit however. A recipe was tried with no sulfur and the propellant would not ignite even with an open flame.

Test data from one of the tests is displayed in table 6-3. Figure 6-1 is a plot of the temperature change for the data in table 6-3. Along with the high energy outputs, the major deciding factors for an optimal propellant was how well the propellant burnt and if it was easy to ignite. A good burning propellant will not spew sparks everywhere but burn consistently and burn up entirely leaving next to no solids behind [11]. Particles in the fluid flow of the nozzle cause multiphase flow. This is not desirable and contributed to a decrease of nozzle efficiency and performance [14]. Out of all the tests, RF4 (Rocket fuel 4, the fourth combination tried) performed well under these requirements.
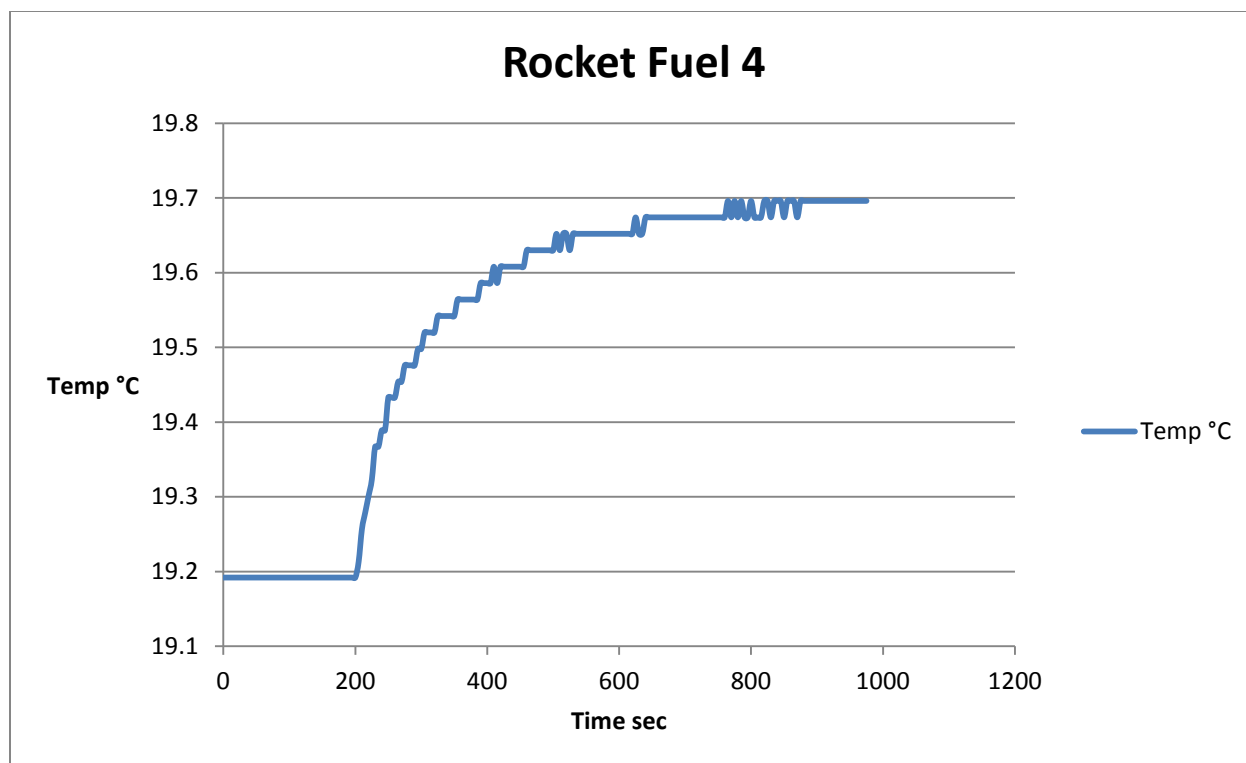
Figure 6-1: Rocket Fuel 4 Plot
Data plot of one of the three RF4 tests.

During ignition, the sample would burn for only a few seconds. The temperature of the water surrounding the bomb will rise almost immediately as seen in 6-1. The sharp increase in temperature is directly after ignition. It would generally take about 10 minutes for the temperature to level off. Once there was no rise in temperature, the difference was recorded and used to calculate the energy output using equation 17.

$$\Delta H = \beta(m_w c_w + m_{ss} c_{ss} - m_{gas} R)\Delta T$$

Table 6-3 Test data of RF4

The propellant settled on was referred to as RF4 (Rocket fuel 4), the fourth combination tried.

Initial Temp °C	19.192	±	0.022	0.1%
Finial Temp °C	19.696	±	0.022	0.1%
Δt °C	0.504	±	0.044	8.7%
Energy Out kJ/kg	7.203	±	0.044	0.6%
Ave Of 3 Tests	6.8	±	0.2	3%

6.3 Uncertainty

From the start, this project was designed and carried out in a way to maximize the precision by which the propellant energy was measured. Attention to detail and consistency between tests contributed to the precision of the student designed and built bomb calorimeter. However, the accuracy achieved was not good enough to use the initial approach of a parabolic curve fit to the energy measurements to locate an optimum. Between tests of different propellant formulations, the energies measures did produce a slight trend but not enough to make any definitive conclusion as to what propellant was truly optimal. David Newey covered this topic a little more in his thesis on this project.

The major contributors to the uncertainty of the calorimeter measurements are the losses due to an imperfect insulating container and the compounding measurement uncertainties of the constants in table6-1. These losses are hard to quantify without a large sum of measurement data to analyze. Unfortunately, not enough tests were conducted to provide a thorough uncertainty analysis.

The time needed to study a theoretical uncertainty was out of the scope of this project in the end but planned for however, in the beginning. Uncertainties were accounted for in the best way possible. The data sets that were taken were analyzed for their averages and standard deviations with decent results.

Chapter 7

Conclusion

7.1 results

The main goal of this project was to narrow down the different chemical formulas for an optimized ammonium nitrate based propellant by evaluating the overall energy produced during combustion.

The initial narrow down process was to use the parabolic curve fit method. This would theoretically find the highest energy possible.   As mentioned in chapter 6, the homemade bomb calorimeter system was not able to produce the precision needed to see the small changes in energy that would result in changing the chemical formula. For this reason the parabolic curve fit method was abandoned.

The initial assumption was that the propellant that released the most energy would be the optimal propellant.   In theory, that would be correct.   In reality, variables such as measurement uncertainties, combustion inefficiency, and particle size clouded the idea that energy output was the best determining factor. High energy output in conjunction with suitable combustion products and ease of ignition were the decisive elements.

7.3 Chosen Propellant Formula

Over all the project was a success and a propellant formula was found and can now be tested for burn rates in preparation for use in a rocket engine.

Table 7-1
Best performing solid propellant formula

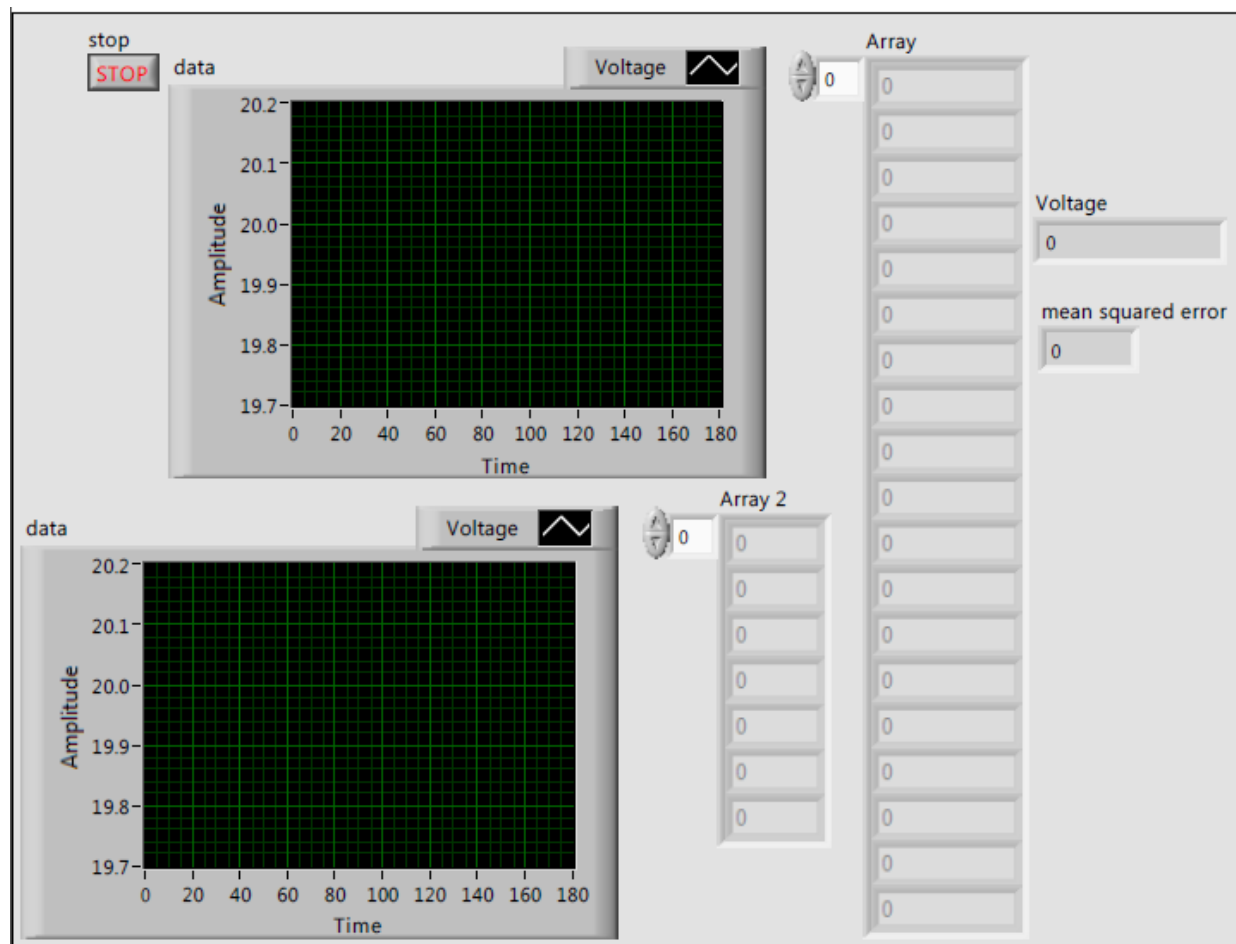| NH4NO3	S	Al	Binder
75.00%	0.66%	19.90%	4.50%

7.3 Future research

There is still a lot of exciting work that can be done to perfect this propellant for use in a rocket engine. Phase stabilization first, followed by burn rate measurements, exhaust gas specific heat ratio and burn temperature are all topics that need researched in order to make a high performing rocket with this propellant.
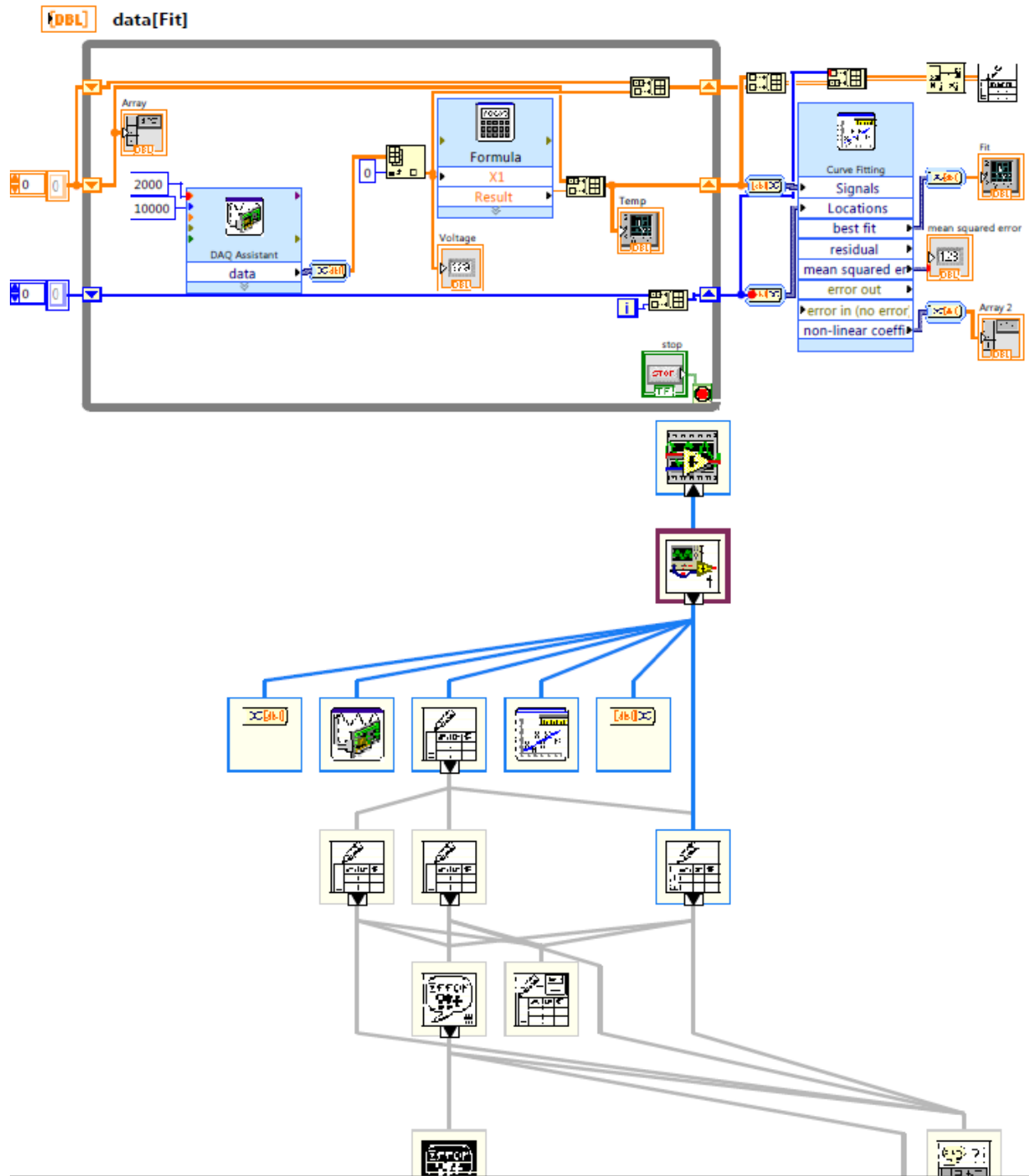
Another branch this research could take would be to mix the industry standard ammonium perchlorate and ammonium nitrate together as the oxidizer in the propellant. This combination of high temperature ammonium perchlorate reactions with the gas generator ammonium nitrate could prove to be a very effective high performing rocket propellant.   In addition, it would be interesting to see how this combination would affect the phase stabilization of ammonium nitrate.

Appendix

American Pyro Supply	Chemical supplier
Firefox enterprises	Chemical supplier

LabVIEW program details

Convert from Dynamic Data2
Convert from Dynamic Data
Converts the dynamic data type to numeric, Boolean, waveform, and array data types for use with other VIs and functions.

DAQ Assistant

DAQ Assistant

Creates, edits, and runs tasks using NI-DAQmx. Refer to the NI-DAQmx Readme for a complete listing of devices NI-DAQmx supports.

When you place this Express VI on the block diagram, the DAQ Assistant launches to create a new task. After you create a task, you can double-click the DAQ Assistant Express VI to edit that task. For continuous measurement or generation, place a while loop around the DAQ Assistant Express VI.

For continuous single-point input or output, the DAQ Assistant Express VI might not provide optimal performance. Refer to the Cont Acq&Graph Voltage-Single Point Optimization VI in examples\DAQmx\ Analog In\Measure Voltage.llb for an example of techniques to create higher-performance, single-point I/O applications.

Write To Spreadsheet File (DBL).vi

C:\Program Files (x86)\National Instruments\LabVIEW 2011\vi.lib\Utility\file.llb\Write To Spreadsheet File (DBL).vi

Write To Spreadsheet File.vi

C:\Program Files (x86)\National Instruments\LabVIEW 2011\vi.lib\Utility\file.llb\Write To Spreadsheet File.vi

Convert from Dynamic Data3

Convert from Dynamic Data
Converts the dynamic data type to numeric, Boolean, waveform, and array data types for use with other VIs and functions.

Convert from Dynamic Data

Convert from Dynamic Data
Converts the dynamic data type to numeric, Boolean, waveform, and array data types for use with other VIs and functions.

Curve Fitting

Curve Fitting
Computes the coefficients that best represent the input data based on the chosen model type.

This Express VI is configured as follows:

Model type: Non-linear
Model description: v*(1-exp(-b*(t-m)))*(1-1/(exp(t-m)/k+1)) +v2
Independent variable: t
Maximum iterations: 500

Convert to Dynamic Data

Convert to Dynamic Data
Converts numeric, Boolean, waveform and array data types to the dynamic data type for use with Express VIs.

Convert to Dynamic Data4

Convert to Dynamic Data
Converts numeric, Boolean, waveform and array data types to the dynamic data type for use with Express VIs.

"calibration.vi History"
Current Revision: 15

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[15] George P. Sutton, *Rocket propulsion elements, Eighth Edition, Pg: 32*

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