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Aviation Research Division
Atlantic City International Airport
New Jersey 08405

# Inerting Concentrations of Fire Extinguishing Agents on Lithium Battery Flammable Gases

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The fire threat within cargo compartments is changing compared to the threat that existed when aircraft class-C cargo compartment requirements were first established. The quantity of lithium batteries being shipped in cargo compartments is increasing each year. Lithium batteries can spontaneously catch fire or undergo thermal runaway where they release a significant quantity of flammable gas composed of hydrogen, carbon monoxide and hydrocarbons.

The objective of this study was to evaluate the effectiveness of Halon 1301 and some of its potential replacements against several flammable gases including lithium battery thermal runaway gases.

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# INERTING CONCENTRATIONS OF FIRE EXTINGUISHING AGENTS ON LITHIUM BATTERY FLAMMABLE GASES

By

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## ABSTRACT OF THE DISSERTATION

# INERTING CONCENTRATIONS OF FIRE EXTINGUISHING AGENTS ON LITHIUM BATTERY FLAMMABLE GASES

by THOMAS CHRISTOPHER MALONEY

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There are many types of commercially available fire extinguishing agents used for a wide range of applications. The specific extinguishing agent used for a given application depends on the fire threat and design criteria. For class-C cargo compartments on aircraft, a gaseous flooding agent is used. Halon 1301 is currently the sole extinguishing agent being used in class-C aircraft cargo compartments. It requires a replacement due to its harm to the environment.

The fire threat within cargo compartments is changing compared to the threat that existed when aircraft class-C cargo compartment requirements were first established. The quantity of lithium batteries being shipped in cargo compartments is increasing each year. Lithium batteries can spontaneously catch fire or undergo thermal runaway where they release a significant quantity of flammable gas composed of hydrogen, carbon monoxide and hydrocarbons.

The objective of this study was to evaluate the effectiveness of Halon 1301 and some of its potential replacements against several flammable gases including lithium battery thermal runaway gases.

Experiments were performed in a 21.15-liter pressure vessel with a gas inlet port, a spark igniter to initiate reactions, a mixing fan, and pressure sensors used to measure gas quantities and quantify pressure rise.

Simulations were conducted in Cantera, a chemical kinetics modeling software, to find laminar flame speed and adiabatic flame temperature for various gas mixtures. Those parameters were used as an estimate to predict inerting concentrations needed for the various gas mixtures. The kinetic, thermodynamic, and transport mechanisms used in the simulations were taken from literature.

First, experiments were performed that compared and verified pressure-rise bell curve profiles for various flammable gases with air. Repeatability experiments were also performed with methane to verify that pressure rise profiles could be repeated with minimal error.

Next, experiments were performed with sub-inerting concentrations of Halon 1301 with hydrogen and sub-inerting concentrations of $CO_2$ with hydrogen to explore any possible over-pressure events.

Finally, experiments and simulations were performed with Halon 1301 and various potential replacements to Halon 1301 to find their inerting concentrations against various individual flammable gases and mixed flammable gases vented from lithium battery thermal runaway. Simulations were also performed to predict the effectiveness of various extinguishing agents at elevated temperatures and decreased pressures.

Initial results showed that the test setup produced repeatable data and that the flammable gas bell curves were consistent with literature. Later, experiments with Halon 1301 and hydrogen produced overpressures for certain concentrations but carbon dioxide with hydrogen did not.

Results from the final portion of this study showed that laminar flame speed and adiabatic flame temperature were reasonable predictors of extinguishing agent inerting concentrations. Halon 1301 was found to be extremely effective against carbon monoxide ignition compared to other extinguishing agents, however it was also least effective against hydrogen than all other flammable gases tested.

Results showed that nitrogen and carbon dioxide were 1.45% and 1.31% more effective against lithium battery gases at sea level pressure than at altitude. When carbon dioxide and nitrogen were compared, at altitude, 28.57% more carbon dioxide than nitrogen was required to inert battery gas on a mass basis. However, on a volume basis, 34.3% more nitrogen was required than carbon dioxide.

For most gas combinations, the greatest concentrations of extinguishing agent was required at a flammable gas equivalence ratio of one. Exceptions to this were mixtures of hydrogen with carbon dioxide, hydrogen with Halon 1301, and 2-BTP/$CO_2$ with hydrogen, methane, ethylene, and battery gas.

Simulations predicted that a much greater quantity of extinguishing agent would be required at elevated temperatures of 200°C compared to 25°C. Up to 7% more Halon 1301, 6.7% more 2-BTP/$CO_2$, 10% more $CO_2$ and 10.9% more $N_2$ would be required to inert battery gas.

At altitude pressure of 25,000 feet, the difference was less pronounced. Experimental results showed that only 1.45% and 1.31% more nitrogen and carbon dioxide was required to inert battery gas. Simulations were conducted to predict the required inerting concentrations of other agents and mixtures. The results also showed that there was an insignificant difference between required inerting concentrations at sea level vs. altitude.

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# 1. Introduction

This chapter provides background information for this study and scientific information useful to understand fire extinguishment and flame inerting. Later in this chapter, the objectives are introduced.

## 1.1. Background and motivation

The purpose of this section is to provide a brief overview of fire extinguishing agents and their usage in industry and on aircraft. This section also introduces lithium batteries and the flammable gas hazard they present along with information about how they are transported.

### 1.1.1. Fire Extinguishing Agents

Fires are a common occurrence and regularly cause major damage throughout the world. For this reason, techniques are necessary to control a fire and minimize damage. There are four main techniques to control a fire. These include cooling, removing fuel, removing oxygen and/or interfering with intermediate chemical reactions. A common method of accomplishing one or more of these is with the use of a fire-extinguishing agent.

The type of fire extinguishing agent used in a given fire depends on the nature of the fire. Fire types are divided into five categories: Class A, Class B, Class C, Class D, and Class K. Class A fires include fires of ordinary combustibles such as wood, cloth, paper, rubber and plastics. Class B fires include flammable liquids and gases. Class C fires are electrical, Class D fires are metal fires and class K fires involve cooking oils and fats [1].

Two categories of extinguishing agents exist. These are total flooding agents and streaming agents. Total flooding agents completely flood an enclosed volume with extinguishing agent to suppress a fire. Streaming agents are used in handheld extinguishers to stream the agent directly onto a fire.

A noteworthy group of extinguishing agents commonly used are called "clean agents". Clean agents are inert gases that do not leave a residue behind and are desirable in circumstances that involve sensitive electrical equipment [2]. They are also frequently used in aviation applications where electrical components need to function properly after an agent is deployed for continued safe operation of an aircraft.

### 1.1.2. Fire extinguishing agents in industry

As mentioned, total flooding agents completely flood an area with extinguishing agent to suppress a fire. Until the early 1990's, Halon 1301 and $CO_2$ were the main total flooding agents available. $CO_2$ was used for normally unoccupied spaces and Halon 1301 was used for both normally occupied spaces and unoccupied spaces. As time continued, more candidate total flooding fire-extinguishing agents were evaluated. They were categorized into five classes: hydroflourocarbons (HFC's), hydrochloroflourocarbons (HCFC's), inert gases, perfluorocarbons, and perfluorinated ketone. Common examples of each of the agents are listed in Table 1.1. In general, HFC's, HCFC's and perflourinated ketone are more effective at extinguishing a fire than inert gases on both a volume and mass basis. Additionally, unlike most HFC's, HCFC's, etc., inert gases are generally stored as a gas instead of a compressed liquid. This brings about the requirement of larger storage tanks. [3]

### 1.1.3. Fire extinguishing agents on aircraft

There are several classes of cargo compartments that are available for use on transport category aircraft. The categories of compartments include Class-A, Class-B, Class-C, Class-D, Class-E and Class-F. Among all of the compartment types, Class-C compartments require a built-in fire extinguishing or suppression system and Class-F compartments allow a built-in system as one of the means to suppress or extinguish a fire. Class-E compartments utilize depressurization, Class-A and B utilize in-person crewmember intervention and Class-D utilizes oxygen starvation.

The two types of cargo compartments that are most widely used around the world are Class-C and Class-E. As discussed, Class-C cargo compartments rely on a fire suppression agent that must meet certain criteria while Class-E compartments rely on depressurization.

For a total flooding fire-extinguishing agent to be used on an aircraft in the United States, EPA SNAP (Significant New Alternatives Policy) approval is required for total flooding in an unoccupied area. Additionally, aircraft fire extinguishing systems are required to meet 14 CFR 25.851 [4]. The common means to satisfy 14 CFR 25.851 is through AC 25.851-1 [5]. AC 25.851-1 also specifies that any new agents should meet a minimum performance standard.

The current performance standard includes a test called the “aerosol can test”, which involves an experiment where agent performance is evaluated against a simulated aerosol can explosion. The simulated aerosol can is made up of a pressurized cylinder of water, alcohol, and propane that is suddenly released in a simulated aircraft cargo compartment that already contains the gaseous extinguishing agent. In order for the agent to perform successfully, it needs to suppress ignition of the flammable mixture.

Halon 1301, also known as $CF_3Br$ or Bromotrifluoromethane is the most commonly used agent in aircraft class-C compartments. On aircraft, it is required to be used at an initial knockdown concentration of at least 5% by volume followed by a maintained minimum concentration of 3% for the remainder of a flight.

As of 1994, Halon 1301 was banned from production due to ozone depletion potential. The extreme effectiveness of Halon 1301 in the unique environment of an aircraft however, has made finding a suitable replacement extremely difficult. As a result, for the last 28 years, aircraft have continued to utilize recycled and stockpiled Halon 1301 that was created before the production ban. However, the European Commission had a cutoff date of 2018 for usage of Halon 1301 in any newly designed aircraft. Therefore, any aircraft with a type-certificate application date 2018 or later requires an alternative suppression agent to replace Halon 1301 in order to operate in Europe. There is an urgent need for the aviation industry to discover and implement alternatives to Halon 1301, and there is much active work ongoing to find these suitable replacements.

In the United States, the class-C cargo compartment became widely used in 1998 when all class-D compartments were required to be converted to class-C. The main reason for the conversion from class-D compartments to class-C was to protect from aerosol can explosions. An additional motivating factor or push for this regulation was driven by the

1996 ValuJet accident where a passenger aircraft crashed into the Florida Everglades due to the ignition of several boxes of chemical oxygen generators.

In recent years, lithium batteries have increased in popularity and have created a new hazard that was previously not a concern when the class-C rule was implemented. The question of whether Class-C compartments should also be certified to suppress lithium battery explosions in addition to aerosol cans, remains to be answered.

Class-E cargo compartments rely on depressurization to reduce the amount of oxygen available to a fire, thereby reducing its intensity and temporarily suppressing it. Specific depressurization procedures are followed which typically require the aircraft to ascend or descend to approximately 25,000 feet and allow the outside atmospheric pressure to equilibrate with the inside class-E compartment pressure. Although class-E compartments can be effective at suppressing a fire, one potential downside of a class-E compartment is the hazard associated with flashover of the compartment upon descent as an influx of oxygen upon descent could cause unburnt accumulated combustible gases to suddenly ignite.

In an aircraft class-C cargo compartment, extinguishing agent concentration is maintained in the compartment with cargo liner barriers that are taped at the seams. There may still be some leakage and additional extinguishing agent is usually added after time to account for losses.

Additionally, within a class-C cargo compartment, there are panels in place to protect against hazards of rapid depressurization. The panels must remain in place to prevent Halon 1301 or alternate fire extinguishing agents, from leaving in the event of a fire. It is therefore important that any pressure rise caused by the ignition of any flammable gases produced in the cargo compartment remain below the pressure threshold that would damage or dislodge the liners or panels. The pressure differential required to disturb the cargo liner or dislodge the blowout panel is 1 psi or less [4]. Therefore, a pressure differential greater than this will compromise the integrity of the cargo compartment and its ability to maintain the design concentration of suppression agent. Compromised liners or panels could allow smoke and gases from the fire to spread to habitable areas of the airplane.

### 1.1.4. Lithium batteries

As mentioned, lithium batteries have become increasingly common and exist in most battery-powered devices, which include cell phones, laptops, tablets, power tools, electric vehicles, etc. Due to their high demand, an increased quantity is transported worldwide.

Although there are many benefits to using lithium batteries over conventional battery chemistries, if overheated, damaged, poorly manufactured, or improperly handled, lithium-ion and lithium-metal cells can undergo a process called thermal runaway. Thermal runaway results in a rapid increase of battery cell temperature and pressure, accompanied by the release of flammable gases.

To reduce the risk of thermal runaway while in an aircraft, a number of transportation rules have been implemented. These rules include shipment at a reduced state-of-charge (SoC), package markings, and a ban from shipment on passenger aircraft. The rules significantly reduce the likelihood of a catastrophic event. Unfortunately, the rules do not provide 100% safety and many companies knowingly or unknowingly ship batteries without regard to the rules.

One of the biggest hazards of lithium battery thermal runaway is the release of flammable gases. A challenge of seeking an extinguishing agent for use with thermal runaway gases is the variability of gas compositions that are emitted from a battery. The composition and quantity of flammable gases varies by the size and specific chemistry of the battery. Some of the more common types of lithium-metal and lithium-ion batteries that exist are shown in Table 1.2. Among the battery cathode chemistries listed, the electrolyte composition can also vary (Table 1.3).

## Lithium battery gases

Two hazards of flammable thermal runaway gases are accumulation of the gases and combustion as they are emitted. In the latter, flammable gases emitted from a lithium battery in thermal runaway will often be ignited by the battery's high temperature, resulting in a fire. However, if conditions are right, the gases will accumulate and potentially cause an explosion. For these reasons, a suitable and adequate fire suppression system may be necessary in certain applications such as transportation of batteries by aircraft, where otherwise uncontrolled fires or explosions could be catastrophic.

Examples of the outcomes from accumulation of flammable lithium battery gases followed by ignition are shown in Figure 1.1 and Figure 1.2. Both figures are from tests conducted at the Federal Aviation Administration Technical Center [7]. In Figure 1.1, an aerosol fire-extinguishing agent was deployed but the concentration was not great enough to prevent the resulting explosion. It was worth noting that only a relatively small number of 18650 lithium-ion batteries had undergone thermal runaway when the explosion occurred. This indicated that much larger battery storage areas or cargo areas would also be a concern with the much larger quantities of batteries that are commonly stored or transported.

Figure 1.2 shows the result of an FAA lithium battery test where an explosion occurred in a full-scale 727 aircraft Class C cargo compartment test [7]. In this test, Halon 1301 was used, but as time went on, explosive gases continued to accumulate and the Halon 1301 fire extinguishing agent concentration continued to recede. Eventually, a spark occurred and caused the explosion. It was unknown what the quantity of Halon 1301 was at the time of the explosion. The explosion caused the panels above the compartment to dislodge and bend upward into the Class-E main deck compartment. The pressure rise was great enough to launch the cockpit door off its hinges and bend the entire wall separating the cockpit from the main deck.

As a final example, in a third experiment performed at the FAA involving the combustion of lithium battery vent gases, 551 lithium-ion 18650 cells were allowed to vent into a 10.8 $m^3$ chamber from a partially closed-off, oxygen-deprived, fire-resistant box. After all the cells had vented, a specific quantity of Halon 1301 was added and then a spark igniter was activated. Out of the two tests that were performed with Halon 1301, the test with 5.28% Halon 1301 had little effect on explosion pressure whereas the test with 10.43% Halon 1301 successfully suppressed combustion (Figure 1.3). [7]

A variety of flammable gas concentrations can be emitted from lithium batteries. The FAA performed experiments to show that the variability in gas concentrations depends on state-of-charge (SoC) as well as chemistry of the batteries. The main flammable gas constituents include hydrogen, carbon monoxide, carbon dioxide and a mixture of hydrocarbons. The hydrocarbons emitted are frequently lumped together and called “total hydrocarbon concentration” (THC). Figure 1.4 shows the major gas species that are emitted from a $LiCoO_2$ 18650 battery. As SoC increases, the volume of gas emitted from lithium batteries also increases as shown in Figure 1.5 for a $LiCoO_2$ 18650 lithium battery. [5]

Lithium-metal batteries are non-rechargeable lithium batteries and lithium-ion batteries are rechargeable. Both are common and both contain an organic compound electrolyte that decomposes when a cell undergoes thermal runaway. The electrolyte consists of a lithium salt dissolved in the organic solvent (Table 1.3). The diversity of organic solvents may cause a variety in the concentrations of exhaust gas constituents. However, as shown, the majority of the components will be made up of carbon, hydrogen, and oxygen.

## Transportation of Lithium Batteries

Lithium batteries are currently shipped by air, ground, and sea. Current regulations forbid the bulk shipment of lithium-ion and lithium-metal batteries aboard passenger aircraft. On cargo aircraft, bulk shipments of lithium-ion cells and batteries are currently required to be shipped at 30% SoC and bulk shipments of lithium-metal cells can be shipped at their normal undischarged state.

Currently, lithium-ion and lithium-metal batteries shipped in or with equipment can be transported in either cargo or passenger aircraft without SoC limitations.

In 2015/2016, when the International Civil Aviation Organization (ICAO) updated their recommended shipment requirements they also commissioned an SAE committee

(SAE-G27) to develop a packaging standard that would ensure the safe transportation of lithium batteries by air. Once the SAE recommendations are complete, it is still to be seen how they will be utilized.

## 1.2. Review of Relevant Concepts

The following section will introduce and discuss analytical and measurement techniques used to evaluate extinguishing agent effectiveness against flammable gases and present some of the experimentally found inerting concentrations from literature for several agent/flammable gas combinations.

### 1.2.1. Pressure Rise and Rate of Pressure Rise from Gas Ignition

When an accumulation of flammable gas ignites in an enclosed space, rate-of-pressure-rise during combustion can have implications to the amount of damage that the particular compartment receives. If the compartment is not able to relieve pressure fast enough, significant structural damage can occur.

A common metric to quantify rate-of-pressure-rise is "deflagration index" as given in equation 1, where $\left(\frac{dP}{dt}\right)_{max}$ is the maximum slope of the time-pressure curve and V is the volume of the vessel.

$$K_G = \left(\frac{dP}{dt}\right)_{max} \times V^{1/3} \qquad 1$$

In a study conducted by Cashdollar et al. [6] it was shown that values for deflagration index varied depending on the size of the pressure vessel used. However, maximum pressure rise was consistent with a slight decrease in pressure rise with increased volume (Table 1.4). For methane, propane, and hydrogen, their results are shown in Table 1.5. The variation in rate-of-pressure-rise with vessel volume was attributed to disturbances that formed in larger vessels because of the change in flame propagation from laminar to turbulent [7].

### 1.2.2. Inerting Concentrations

"Inerting concentrations" specify the volume of fire extinguishing agent necessary in a given volume of flammable gas required to prevent ignition or keep the result of ignition below a hazardous threshold. Methods to quantify inerting concentration can be placed into two categories: experimental and computational. Many studies combine both methods to gain further reaction insight.

### Equivalence Ratio

To find the minimum inerting concentration for an extinguishing agent, it is necessary to know the worst-case concentration of flammable gas that it should be mixed with. Maximum pressure rise of combustion for gases such as methane and hydrogen generally occurs near an equivalence ratio of one [8], [9]. It was therefore expected that the greatest quantity of extinguishing agent would also be required at a unity equivalence ratio.

### Experimental Methods of Determining Inerting Concentrations

Experimental studies to find inerting concentrations generally involve mixing various compositions of flammable gases and agents followed by the introduction of an ignition source. The behavior of the resulting event is then observed to determine if pre-determined flammability criteria are met.

Some of the experimental methods to demonstrate flammability include: upward flame propagation, downward flame propagation, pressure rise in an enclosed vessel, and a heptane cup burner. Table 1.6 shows examples of some industry standard test methods used to find flammability limits.

In an upward flame propagation test, a gas mixture is ignited at the bottom of a specific size tube and the mixture is considered flammable if flames propagate to the top of the tube. Similarly, the downward flame propagation test requires flames to propagate to the bottom of a tube when ignited on the top [6].

Pressure rise criteria to demonstrate flammability has been used extensively by the FAA Technical Center's Fire Safety Branch in the past. This method involves an enclosed, pressure-tight vessel, a pressure transducer, a fan, and a spark igniter. Specific volumes of gases are introduced into the pressure vessel. The volumes are determined with the assumption of ideal gas behavior, which allows volume to be determined from a change in pressure. Once the desired mixture is present and well mixed from the fan, a spark is activated. In this method, gas mixtures are considered flammable if pressure in the vessel increases beyond a predefined threshold.

A pressure rise threshold of 5% is frequently used to define flammability [10]. At sea level pressure of 14.7 psia, this would equate to a .735 psi pressure rise. This pressure rise was similar to what had been shown by the FAA to be a hazard in a 737 aircraft cargo compartment [4], (Figure 1.6). Therefore, a flammability threshold of 5% may be most relevant to experiments related to aircraft cargo compartment applications.

Varied flammability limit results can be found in literature for given quantities of flammable gases. For example, in a study presented by Zabetakis, methane was shown to have a lower flammability limit according to upward flame propagation that was 1.2% v/v lower than the flammability according to downward flame propagation [11].

Due to variability of flammability results, it is important to choose a flammability test method most representative of each specific real-life situation. Aircraft cargo compartments are designed to tolerate a certain quantity of flames but they are not designed to tolerate those flames after an over-pressure event has occurred. Therefore, pressure-rise flammability criteria may be most relevant to evaluate extinguishing agent inerting concentrations in aircraft cargo compartments.

## Effect of Initial Temperature and Pressure on Flammability Limit

The initial temperature and pressure of a mixture can affect its flammability and the minimum spark energy required to ignite the mixture.

Mendiburu et al. [12] compiled several literature sources that gave an overview of the temperature dependence of gases on flammability limits. In general, as initial mixture temperature increased, the lower flammability limits of the mixtures also decreased. Some of the gases included in the studies included methane, ethylene, hydrogen and carbon monoxide as well as others. All of the gases demonstrated an increased envelope of flammability at higher temperatures.

Liu et al. [13] performed experiments to show the effect of initial pressure on hydrogen flammability. Their results showed that increased pressures led to an increase in flammability envelope. Similarly, Huang et al. [14] showed this same trend for methane,

ethane, and propane. Both studies used pressure-rise criteria for flammability and were performed at pressures above ambient.

At pressures below ambient such as altitude, a similar trend has been observed. Rehn [15] showed that the lower flammability limit of hydrogen decreased at pressures below ambient. In an aircraft, this could lead to an increase in hazard.

## Computational & Analytical Methods of Determining Flammability Limits

Computational studies to find flammable limits or inerting concentrations, generally involve the modeling of parameters such as flame speed and adiabatic flame temperature to determine if a mixture is flammable. For extinguishing agents mixed with flammable gases, these studies can also highlight different intermediate reactions to determine which intermediate reactions have the greatest impact on extinguishment.

Analytical methods can be used as well. Le Chateliers formula is a common analytical tool used to predict flammability limits of mixtures (equation 2), where $\mathrm{LFL}_{\mathrm{mix}}$ is the lower flammability limit (LFL) of the mixture, $\mathrm{x}_{\mathrm{i}}$ is the mole fraction of the ith component and $\mathrm{LFL}_{\mathrm{i}}$ is the LFL of the i-th component. However, this equation was not designed to account for the usage of fire extinguishing agents.

$$\mathrm{LFL}_{\mathrm{mix}} = \frac{1}{\sum \frac{\mathrm{x}_{\mathrm{i}}}{\mathrm{LFL}_{\mathrm{i}}}} \qquad 2$$

To extend the usability of the formula, Shigeo et al [16] created an extended Le Chatelier's formula to predict the flammability limits of various flammable gases diluted with carbon dioxide. They modified Le Chatelier's formula and incorporated experimentally found parameters to develop a new equation that gave good agreement with experimental results. The new formula can be useful for known extinguishing agents but would require constant modification as new extinguishing agents are created. Additionally, this formula may not be able to account for cases where the agent extensively breaks down and reacts.

Laminar flame speed can be defined as the speed at which combustion propagates through unburned reactants [17]. It is the sum of the local burning velocity and the unburned gas velocity. Consequently, relative to a fixed point, the actual speed that a flame appears to be moving will be larger than the calculated flame speed because expansion of hot gases behind the flame front are not taken into account as part of flame speed determination [18]. Typically, a flame speed of about 3cm/sec to 5cm/sec is generally accepted as the limit of flammability [19], [20] and allows simulations to be conducted computationally to predict inerting concentrations of extinguishing agents with flammable gases.

Constant volume adiabatic flame temperature can be defined as the temperature that a flame achieves without any heat transfer, work, or change in total energy. Typically, an adiabatic flame temperature of 1400K to 1600K has been shown to be a good approximation of the flammability of a gas mixture [21], [22].

Additional methods to compute flammability limits exist based on fits to experimental data without much regard to theory of combustion, flame propagation and flame extinction. Li, Liu et al. compiled a list of seven different studies with different “black box” approaches. [23]

### 1.2.3. Work done with various extinguishing agents

Throughout the years, various experimental and computational studies have been conducted with extinguishing agents to evaluate their behavior with various flammable substances. Extinguishing agents currently of interest to the aviation community include Halon 1301, 2-BTP, 2-BTP blended with $CO_2$ (also called Verdagent), $N_2$ and Aerosols. There are a few main mechanisms by which gaseous fire extinguishing agents work. Agents absorb heat, push away and thereby reduce the quantity of fuel and oxygen, and sometimes, certain agents also interfere with intermediate chemical reactions.

#### Halon 1301

Due to the phase-out of Halon 1301, the amount of research performed to understand how it works has decreased over the years. However, a good amount of research was performed before the phase-out.

In 1975, Ford published a report summarizing experiments that had been performed to date with Halon 1301. Twenty-eight test series were included and describe the effect of Halon 1301 on a wide range of flammable materials including flammable gases. They also compared methods of application, conditions of application, as well as other relevant variables. [24]

Table 1.7 gives a summary of some experimentally found inerting concentrations for Halon 1301 with some flammable gases. As shown, the greatest quantity of Halon 1301 was required for hydrogen followed by ethylene, battery gas and methane.

In 1961, Creitz showed that Halon 1301 was significantly more effective on a diffusion flame when it was added to the surrounding air compared to cases where it was added to the fuel. Interestingly, he also showed that $N_2$ showed the opposite trend. It was significantly more effective when added to fuel. For $H_2$, and $CH_4$, 17.7% and 1.5% Halon 1301 was required respectively for agent added to surrounding air. When the agent was added to the fuel, 58.1% and 28.1% Halon 1301 was required to inhibit combustion. For $H_2$ and $CH_4$ with $N_2$ agent, 94.1% and 83.1% were required when added to surrounding air and 52.4% and 51% were required when added to the fuel. For the application of fire extinguishing agents on aircraft, agent added to the surrounding air is more relevant. This study also implied that the effectiveness of extinguishing agents was dependent on how well it was mixed with the flammable gases.

Casias and McKinnon performed simulations with $CF_3Br/C_2H_4$ flames to rank the effectiveness of $CF_3Br$ extinguishing mechanisms. They used simulated flame speed as their ranking criteria. Mechanisms that had a larger effect on simulated flame speed were ranked as more effective. Their results showed that the mechanism effectiveness ranked as follows [25]:

1: "H-atom trapping" in $H + CF_3Br = CF_3 + HBr$

2: "H-atom scavenging" in $H + HBr = H_2 + Br$

3: Endothermic dissociation of $CF_3Br$ in $CF_3Br = CF_3 + Br$

4: Free-radical termination in $Br + HO_2 = HBr + O_2$

Halon 1301 contains bromine and fluorine, which are both known to be effective as flame inhibitors. However, bromine is known to be more effective [26], [27]. As shown in the reactions above, the bromine and fluorine in Halon 1301 react with various intermediate gas species. They react with significantly less heat release than the reactants would have achieved if the agents were absent.

Linteris et al. showed that for lean flames, addition of Halon 1301 or 2-BTP could increase the overall reaction rate rather than decrease it [26]. They showed that radical composition and flame speed are not reduced as much from 2-BTP addition as they are from Halon 1301 addition.

Many studies showed that the addition of halogenated hydrocarbons to flammable mixtures can widen the flammability limits of some mixtures [28], [29], [30], [31]. Shebeko et al. showed that the pressure rise and rate-of-pressure-rise can increase with the addition of halogenated hydrocarbons [31].

Researchers also showed that the addition of water vapor to a mixture can significantly affect flammability limits [32] and increase the flame speed of mixtures with Halon 1301 and 2-BTP [33].

## 2-BTP

Similar to Halon 1301, 2-BTP reacts with intermediate combustion species to slow overall reaction rate. Tests have shown that 2-BTP is effective at suppressing a cup-burner but at lower concentrations, 2-BTP can react exothermally and promote combustion [34].

In 2015, Burgess, Babushok et al. did an extensive literature review and found that there had not been any previous efforts to characterize the kinetics of 2-BTP flame inhibition [34]. They described the kinetics of bromine and fluorine reactions and their role in interrupting intermediate chemical reactions. In particular, they described the effectiveness of fluorinated intermediates at slowing reactions with the caveat that high enough temperatures would destabilize the intermediates causing them to decompose [34].

As a result of decomposition of 2-BTP and resulting promotion of heat release, blends of 2-BTP with $CO_2$ were studied.

## 2-BTP Blended with Carbon Dioxide

To overcome the overpressure experienced with limiting concentrations of 2-BTP, research was conducted with blends of fire extinguishing agents. Linteris et al. [35] performed experiments and simulations to determine how a 50/50 blend by weight of 2-BTP and $CO_2$ would behave against moist propane. Their experimental results showed that a volume fraction of .18 "should" be sufficient to prevent combustion in the aerosol can test performance standard. Their simulations predicted a similar inerting concentration of .19.

## Carbon Dioxide

Various studies have also been conducted to evaluate the effectiveness of $CO_2$ against flammable gases. Unlike Halon 1301 and 2-BTP, $CO_2$ does not react with intermediate species in the same way to interrupt combustion. Instead, $CO_2$ absorbs heat and displaces oxygen and fuel. A certain quantity of fuel and oxygen are necessary for combustion. The heat capacity of $CO_2$ plays a role in its effectiveness. It is able to act as a heat sink to absorb energy that would have otherwise progressed combustion.

Table 1.8 shows results from literature of the effectiveness of $CO_2$ at inerting various flammable gases. Coward and Jones [36] showed that approximately 23% $CO_2$ was required to prevent methane combustion while Liao et al. [37] showed that 28.6% was required. Coward and Jones also compiled a literature survey where inerting concentrations from five sources varied from 17% to 25% $CO_2$ to suppress methane combustion depending on which flammability criteria that was used.

Similarly, tests were performed with hydrogen where they showed that in an upward flame propagation test with a 6-foot tube that was 2 inches in diameter the inerting concentration of $CO_2$ was about 61%. When tests were repeated with downward propagation in a 65cm long and 5cm diameter tube, 56% $CO_2$ was required for inertion. [36]

Similar experiments were performed with CO. Upward flame propagation criteria in a 6 foot, 2 inch diameter tube showed 53% $CO_2$ was necessary for inertion [36].

## Nitrogen

Table 1.9 shows results from literature of the effectiveness of $N_2$ at inerting various flammable gases. $N_2$ behaves in a similar manner to $CO_2$. It displaces oxygen and absorbs heat.

Results of an upward flame propagation test that utilized a 6-foot tube with a 2-inch diameter showed that 75% additional nitrogen added to air was required to suppress hydrogen combustion [38]. Downward flame propagation tests in a tube that was 65cm in length and 5cm diameter gave similar results [39].

The same experiments were performed with CO. Upward flame propagation criteria in a 6 foot, 2 inch diameter tube showed 68% nitrogen was necessary [38].

Coward and Jones [36] conducted a literature survey in which they compiles flammability limit data from various sources. For methane and nitrogen, they showed that the inerting concentrations varied from 27% $N_2$ to 37% $N_2$ depending on the method that was used. The 27% concentration corresponded to a Hempel pipette and the 37% concentration corresponded to upward propagation in a 5cm diameter tube. Between those two measurements were a 2.7cm diameter tube, a 2.6-liter bomb, and a 2-liter sphere. Additional methane results can be found in references: [40], [41], [37] and found in Table 1.9.

## Depressurization

Depressurization has the direct effect of reducing the amount of available oxygen in an environment. Rehn [15] performed experiments with hydrogen combustion at altitude and showed that the lower flammability limit decreases at higher altitudes.

## Aerosol

Aerosol fire extinguishing agents consist of solid particles suspended in an inert gas, such as $N_2$ and/or $CO_2$. Aerosol agents can be released from a solid compound that is activated and burns to release the agent or they can be released from a compressed vapor. According to the National Fire Protection Association, condensed aerosols release solids less than 10micrometers in diameter. [42]

Because of the small size of condensed aerosol particles, they absorb a greater amount of heat per mass than dry powders. Generally, the solid particles are potassium based and the mixture after dispersion may contain molecules of $K_2CO_3$, KOH, $KHCO_3$, KCl, $H_2O$, CO, C, $K_nO_m$ and/or $N_xO_y$ as well as $N_2$ or $CO_2$ as was previously mentioned. [43]

Agafonov, Kopylov, et al. reported experiments that showed the level of oxygen depletion that solid aerosol activation can cause in a .53m3 chamber. In that size vessel, they showed that the oxygen concentration can decrease to a value as low as 16.4% when the density of aerosol is .1kg/m3 within the vessel. These results indicated that condensed aerosol fire-extinguishing agent also has the effect of reducing available oxygen in an environment. [43]

Zhang, Ismail, et al. [44] performed a review on various effectiveness parameters associated with aerosol fire extinguishing agents. They showed that certain solid particles could reduce the temperature of a hydrogen-air flame by 750°C at concentrations of 100g/$m^3$ or 525°C at concentrations of 60g/$m^3$ when the particles are 100% KOH. They also described the health hazard of particle inhalation. Because of the small size of particles, they are capable of causing respiratory diseases.

## 1.3. Objective

The primary objective of this study was to evaluate the effectiveness of various fire extinguishing agents against individual flammable gases as well as a mixture of flammable gases that were representative of the composition emitted from a lithium-ion battery in thermal runaway. The focus of the study was aircraft cargo compartments but the information should be useful in any room or compartment where flammable gases must be suppressed.

An additional objective was to find correlations between the inerting concentrations of individual flammable gases compared to thermal runaway battery gases. This would provide insight into which individual gases were most significant and difficult to control in battery gas mixtures.

Objectives were accomplished mainly through experimental results, however, simulations were found to be a useful resource to help select starting points for gas mixtures and obtain a general understanding that helped steer the design of experiments.

Table 1.1: Common Halon 1301 Replacement Total Flooding Agents

| **HFC** | **HCFC** | **Inert gases** | **Perflouroinated Ketone** |
|---|---|---|---|
| FM-200 | NAF-S-III | Inergen | Novec 1230 |
| FE-25 | | Argonite | |
| FE-13 | | Proinert | |
| | | Argotec | |
| | | NN100 | |

Table 1.2: Types of Lithium Batteries [45], [46]

| **Lithium-Ion** |
|---|
| Lithium Cobalt Oxide ($LiCoO_2$) |
| Lithium Manganese Oxide ($LiMn_2O_4$) |
| Lithium Nickel Manganese Cobalt Oxide ($LiNiMnCoO_2$) |
| Lithium Iron Phosphate ($LiFePO_4$) |
| Lithium Nickel Cobalt Aluminum Oxide ($LiNiCoAlO_2$) |
| Lithium Titanate ($Li_2TiO_3$) |
| **Lithium-Metal** |
| Lithium Polycarbon Monofluoride (LiCFx) |
| Lithium Manganese Dioxide ($LiMnO_2$) |
| Lithium Iodine (LiI) |
| Lithium Sulfur Dioxide ($LiSO_2$) |
| Lithium Thionyl Chloride ($LiSOCl_2$) |

Table 1.3: Organic Solvents used in Lithium Battery Electrolytes

| |
|---|
| Ethylene carbonate ($C_3H_4O_3$) |
| Diethyl carbonate ($C_5H_{10}O_3$) |
| Dimethyl carbonate ($C_3H_6O_3$) |
| Propylene carbonate ($C_4H_6O_3$) |
| Dimethoxyethane ($C_4H_{10}O_2$) |
| Gamma-butyrolactone ($C_4H_6O_2$) |

Figure 1.1: Cargo Container Explosion Caused by Lithium Battery Vent Gases

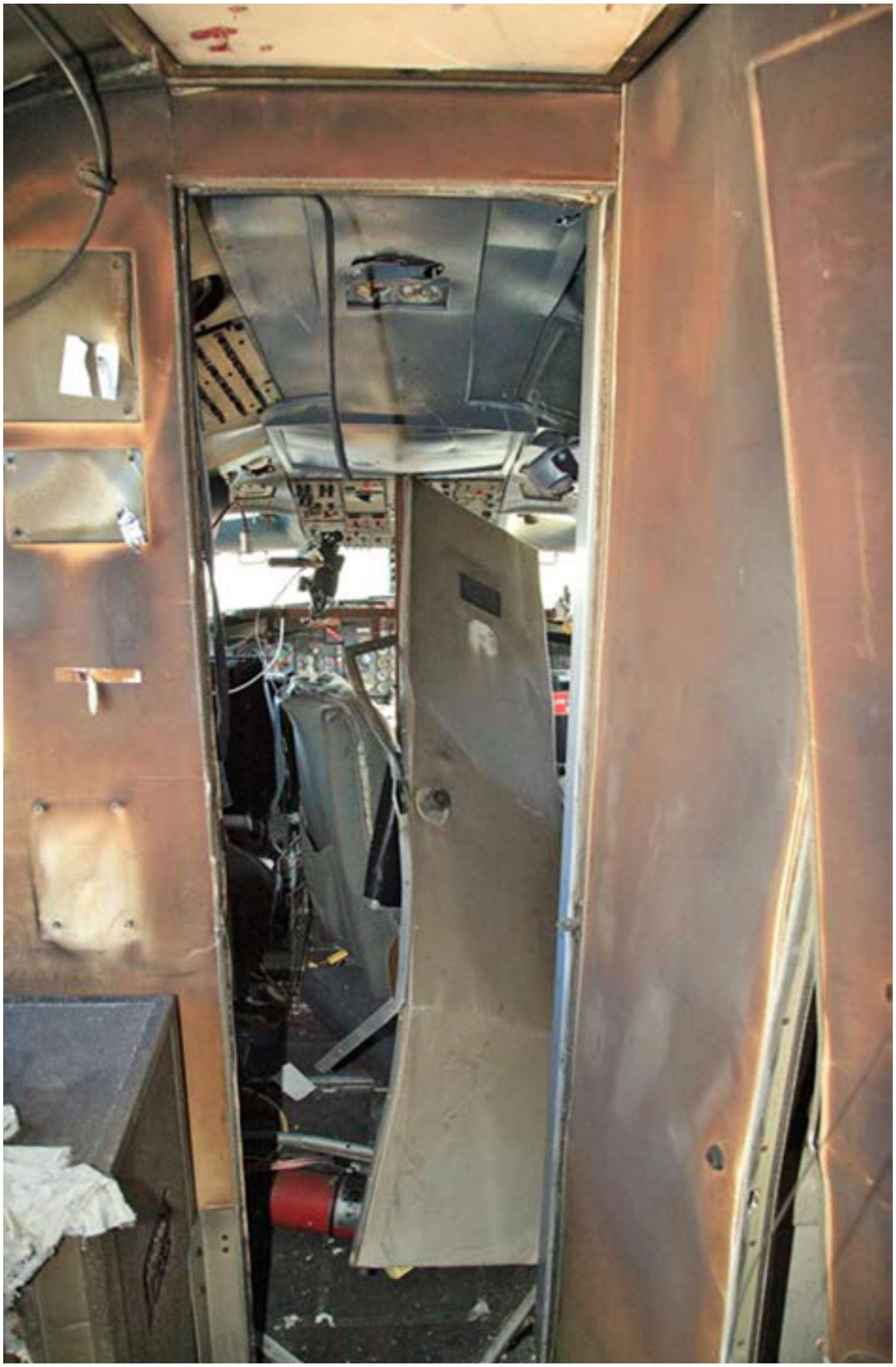
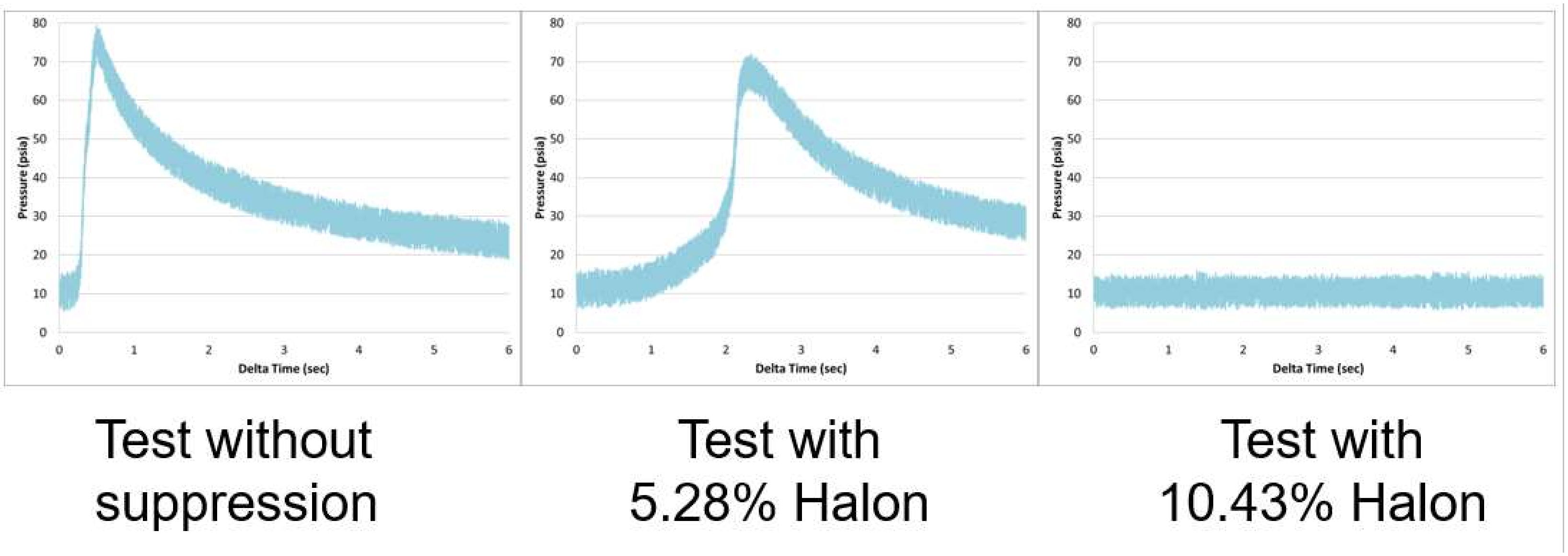


Figure 1.2: Aftermath of Explosion of Cargo Compartment from Lithium Battery Vent Gases



Test without suppression

Test with 5.28% Halon

Test with 10.43% Halon

Figure 1.3: FAA Test Showing the Inerting Effect of Halon 1301 against Lithium Battery Gases [5]

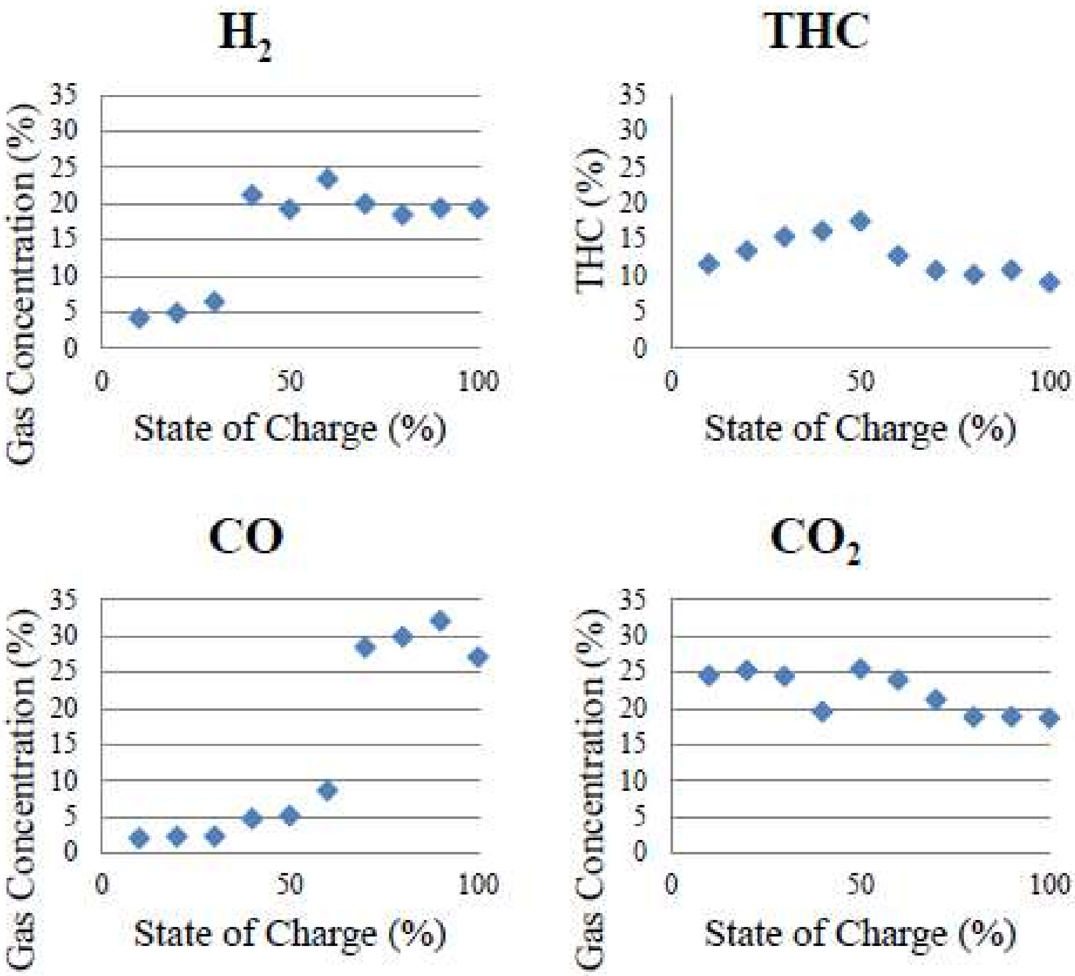


Figure 1.4: Major Gas Species Concentrations for $LiCoO_2$ 18650 Batteries [5]

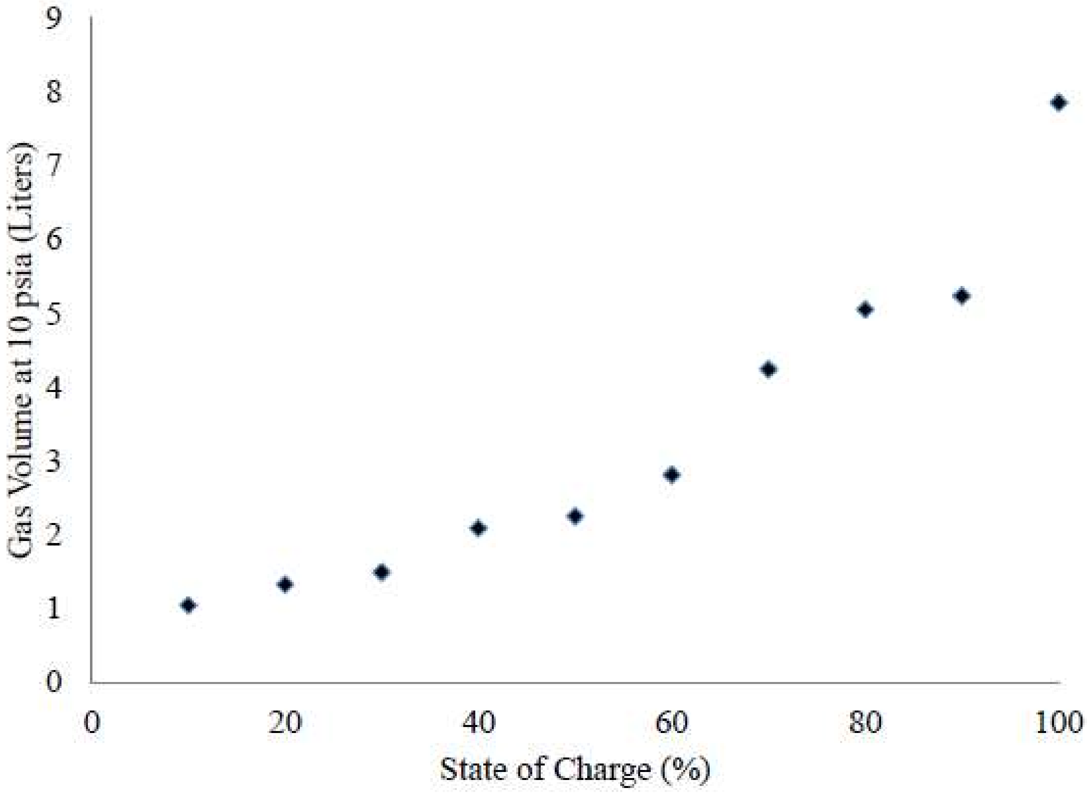


Figure 1.5: Variation in Gas Volume Emitted from a $LiCoO_2$ 18650 Battery with SoC [5]

Table 1.4: Pressure Rise for Methane, Propane, and Hydrogen

| | **Methane** | **Propane** | **Hydrogen** |
|---|---|---|---|
| *20 liter chamber* | 105.9 ± 1.45 psi | n/a | n/a |
| *120 liter chamber* | 108.78 ± 1.45 psi | 118.9 ± 2.9 psi | 103 ± 1.45 psi |
| *25,500 liter chamber* | 95.7 ± 1.45 psi | 113.1 ± 7.25 psi | n/a |

Table 1.5: Deflagration Index for Methane, Propane, and Hydrogen

| | **Methane** | **Propane** | **Hydrogen** |
|---|---|---|---|
| *20 liter chamber* | $957 \pm 29 \frac{psi}{m \cdot sec}$ | n/a | n/a |
| *120 liter chamber* | $1334.4 \pm 43.5 \frac{psi}{m \cdot sec}$ | $2176 \pm 290 \frac{psi}{m \cdot sec}$ | $18275 \pm 1015 \frac{psi}{m \cdot sec}$ |
| *25,500 liter chamber* | $1595.4 \pm 116 \frac{psi}{m \cdot sec}$ | $5802 \pm 1450 \frac{psi}{m \cdot sec}$ | n/a |

Table 1.6: Methods of Determining Flammability Limits [7]

| ***Test Name*** | **Ignition Vessel** | **Ignition Source** | **Criterion** |
|---|---|---|---|
| *EN 1839(T)* | Vertical glass tube | Spark | Visually observed flame propagation of at least 100mm |
| *EN 1839(B)* | 14 liter pressure vessel | Fusing wire | 5% pressure rise |
| *ASTM E 681-01* | 5 liter glass flask | Spark (.4 second duration) | Flame propagation of 13mm |
| *DIN 51 649, part 1* | Vertical glass tube | Spark (.5 second duration) | Flame detachment |

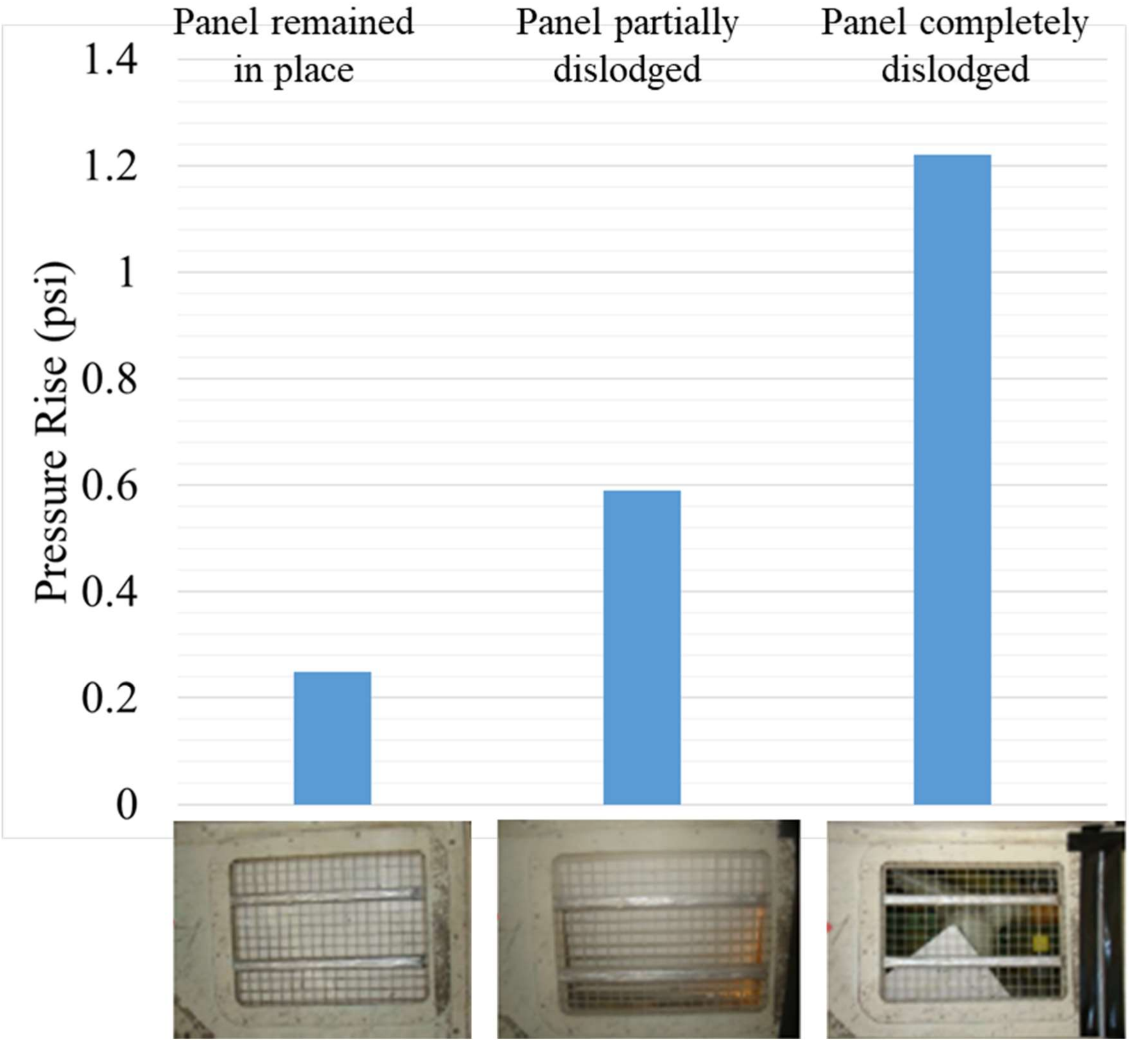


Figure 1.6: Effect of Pressure Rise on an Aircraft Cargo Compartment

Table 1.7: Halon 1301 Inerting Concentrations in Literature for Various Flammable Gases. % v/v Halon 1301 Required: Tubular Flame Method: [37], 21 Liter Combustion Sphere: [10], Visual Upward Flame Propagation: [47]

| | **[37]** | **[48]** | **[10]** | **[47]** |
|---|---|---|---|---|
| *Hydrogen* | n/a | 28.55 | 26.72 | 28 |
| *Methane* | 6.15 | 7 | n/a | n/a |
| *Ethylene* | n/a | 12 | n/a | n/a |
| *Battery Gas* | n/a | n/a | 8.59 | n/a |

Table 1.8: $CO_2$ Inerting Concentrations in Literature for Various Flammable Gases at an Equivalence Ratio of one. % v/v $CO_2$ Required. Source [36] with Methane was Upward Flame Propagation with a Tube that was 7' Length, 10" Diameter, Source [37] was Visual Upward Flame Propagation, Source [36] with Hydrogen at 56% was Downward Flame Propagation, Source [38] was with Hydrogen at 61% and Upward Flame Propagation. Source [36] with CO was Upward Flame Propagation. Source [49] was Downward Flame Propagation.

| ***phi=1*** | **[36]** | **[37]** | **[49]** | **[38]** |
|---|---|---|---|---|
| *Hydrogen* | 56 | n/a | n/a | 61 |
| *Methane* | 22.97 | 28.59 | n/a | n/a |
| *Ethylene* | n/a | n/a | 41 | n/a |
| *CO* | 53 | n/a | n/a | n/a |

Table 1.9: $N_2$ Inerting Concentrations in Literature for Various Flammable Gases at an Equivalence Ratio of one. % v/v $N_2$ Required., Source [41] was a Tubular Flame Burner, Source [37] was a Tubular Flame Burner, Source [50] was Downward Flame Propagation, Source [38] was Upward Flame Propagation, Source [49] was Downward Flame Propagation

| | **[36]** | **[40]** | **[41]** | **[37]** | **[50]** | **[38]** | **[49]** |
|---|---|---|---|---|---|---|---|
| *Hydrogen* | n/a | n/a | n/a | n/a | 75 | 75 | n/a |
| *Methane* | 36.73 | 37.887 | 40.08 | 40.627 | n/a | n/a | n/a |
| *Ethylene* | n/a | n/a | n/a | n/a | n/a | n/a | 50 |
| *CO* | 68 | n/a | n/a | n/a | n/a | n/a | n/a |

# 2. Experimental and Simulation Setup

Tests were conducted in a 21.15 liter, nearly spherical pressure vessel (Figure 2.1). The vessel was constructed of steel and had a closing lid with an O-ring that allowed it to be completely sealed. It utilized a Welch 1405 vacuum pump to draw down pressure and a spark igniter for the gas ignition source. It was equipped with various ports for gas insertion and transducer attachment.

Additional equipment included a 12 volt, 3-inch computer fan to mix gases together, a piezo electric pressure sensor for measuring rapidly rising ignition pressures, and a 0 to 15psia pressure transducer that measured partial pressures and was used to quantify gas volumes as they were introduced through a gas inlet port.

## 2.1. Pressure and Temperature

Pressure was measured with two different devices. An Omega 0 to 15psia pressure transducer was used for partial-pressure/gas-concentration determinations and a Kistler 0 to 203.1psi (0-14bar) piezo electric pressure sensor was used to measure pressure increases caused by ignition. To ensure gas volumes were accurately calculated, the volume of the vessel was determined by filling it with water utilizing a mL scale graduated cylinder. The exact volume of the pressure vessel was measured to be 21.154 liters.

An room temperature vulcanizing (RTV) silicone layer of 1mm was placed on the piezo electric sensor to prevent interference from combustion temperatures (Figure 2.2). Krause et al [51] had previously shown that the addition of an RTV layer onto a piezoelectric sensor can reduce its thermal shock. Similar to the results obtained by [51], Figure 2.3 demonstrated the difference between the sensor with RTV and without RTV from experiments conducted in this study.

A 1/16th inch sheathed, ungrounded type-k thermocouple was used to verify an ambient temperature of 25°C ± 3°C in each test.

## 2.2. Gases

Gases used in this study were purchased from various sources. Table 2.1 provided the purities of the various gases. An additional bottle gas mixture was used to represent gas vented from a lithium battery in thermal runaway (Table 2.2).

2-BTP extinguishing agent was used some of the tests and added from a handheld extinguisher as later described in Section 2.6. A solid aerosol fire-extinguishing agent was also used in some of the tests. The method of its usage is also described later in Section 2.6.

## 2.3. Ignition source

A 10,000 Volt, 23 mA spark igniter was used to ignite flammable mixtures within the vessel. The igniter power was delivered through a Macromatic timing relay set for 0.5 seconds. 0.5 seconds was selected based on industry standard: DIN 51649, as well as previous FAA research [15]. A 5mm spark gap was chosen based on visual spark consistency and its usage in SAE-AS6413.

## 2.4. Data processing

Data from the thermocouple and Omega pressure transducer, used for volume determination, was collected on an Omega DAQ-56 at 1 Hz and data from the piezo-electric pressure sensor was collected on a Data Translation DT8824 DAQ at 4800 Hz. Omega DAQ-56 data was collected with prepackaged Personal DaqView software and Data Translation DAQ data was collected with QuickDAQ software. All data was exported to Microsoft Excel for analysis.

## 2.5. Simulations Setup

Simulations were performed to assist in selection of gas concentrations to perform experiments and to predict required extinguishing agent inerting concentrations at elevated temperatures for which experiments could not easily be performed. Simulations were performed in Cantera utilizing Python. A mixture-averaged diffusion approximation was used as well as “slope” and “curve” values of .05 and .05. These parameters were determined through a series of simulations designed to determine the effect that they had on the accuracy of the model and computation time of the model. A series of simulations showed that the difference in calculated flame speed and adiabatic flame temperature between results derived from mixture averaged diffusion and multi-component diffusion created a difference in solutions that ranged between .05% and .6% from each other. However, the time required for the multi-component diffusion assumption was up to 60 times greater than the results derived from the mixture averaged diffusion assumption (Figure 2.4).

As shown in Figure 2.5, when “slope” and “curve” values were varied, there was a gradual decrease in computation time to roughly 50% of the time required at the finest grid. However, flame speed and flame temperature varied beyond what was considered acceptable in this study (Figure 2.5 and Figure 2.6). It was therefore decided to maintain a fine grid with “slope” and “curve” parameters of .05 for further simulations.

Thermodynamic, kinetic, and transport parameters including those for Halon 1301 and 2-BTP were taken from the list of values compiled by [34]. The compiled list consisted of mechanisms created by over 100 individual sources.

All simulations were performed at a temperature of 25°C and a pressure of 14.7psia unless otherwise specified. To verify the validity of the simulations and that the program was being used properly, data from the model was compared to flame speeds previously generated by several literature sources (Figure 2.7).

Before running experiments with particular extinguishing agent concentrations and flammable gas concentrations, simulations were conducted to find the variation of computed flame speed with quantity of extinguishing agent for fixed flammable gas equivalence ratios. Mixtures with predicted flame speeds of approximately 2cm/sec were used as initial guesses in the spark igniter flammability experiments. (Figure 2.8)

## 2.6. Overall test procedure

In all tests, temperature was allowed to equilibrate to 25°C ± 3°C. Tests were performed according to the following procedure. First, the pressure vessel was thoroughly purged with dried shop air at 120psi through a ¼” tube for at least 10 to 15 minutes. Next, the pressure vessel was vacuumed down to 1 psia or lower. The mixing fan was then initiated and appropriate quantities of flammable gases were added to the vessel. The appropriate amount of fire suppression agent was then added followed by the appropriate amount of air, which brought the vessel up to 14.7 psia. Figure 2.9 showed an example of what a typical test sequence looked like.

Once appropriate gases were added to the vessel, the mixing fan was turned off, high-speed pressure recording was initiated, and after 10 seconds, the 0.5 second spark was activated. After each test, the vessel was immediately, once again, flushed for 10 to 15 minutes with dry compressed air to purge reaction products and prepare for a subsequent test.

When the battery gas mixture was used, the bottle was rolled and tilted repeatedly for several minutes to mix the gases within the bottle and provide a greater mixture uniformity.

2-BTP was extracted from a handheld fire extinguisher and added to the vessel before an equal mass of $CO_2$ was added to create a 50/50 mix by mass. To measure the necessary mass of 2-BTP, a ¼” nominal diameter plastic tube was calibrated with a mL scale syringe to determine how many mL were in each linear inch of tubing. As shown in Figure 2.10, the tube was attached to the 2-BTP extinguisher. To accurately measure a desired quantity of 2-BTP, the tube was partially filled to an appropriate height with a layer of nitrogen gas at the top of the tube. The 2-BTP was then slowly bled into the vessel and the change of height within the tube indicated the quantity of 2-BTP that entered the vessel. The fittings on the exterior of the vessel were then heated with a heat gun to ensure that all

2-BTP vaporized into the vessel. The value for 2-BTP density that was used was 1.6598 g/mL.

Next, after the 2-BTP was allowed to vaporize within the vessel with assistance from the mixing fan for approximately 10 minutes, an equal amount of $CO_2$ was added utilizing pressure increase to indicate mass added. It was recognized that the density of $CO_2$ varied with pressure, so a density vs. pressure curve was used to accurately quantify the $CO_2$ that was added at the pressure that the vessel was currently at.

A solid aerosol extinguishing agent was used in several tests. The aerosol was activated by heat. Two different methods were utilized to apply heat to the agent. These methods were heat conduction and by utilization of a spark. The initial heat conduction method allowed the gaseous agent to pass through an externally attached port, as shown in Figure 2.11. To start, the metal tube was disassembled and the pre-determined mass of the solid aerosol (Figure 2.12) was added to the port configuration and the port was then re-assembled and sealed. A torch was then applied to the outside of the externally attached port to heat the aerosol to its activation temperature. Once activated, the pressure in the 21.15-liter vessel increased a fixed amount. The pressure rise indicated the approximate volume of aerosol that was added to the vessel. The bottled air was then applied to the end of the tube to fill the vessel to 14.7 psia while simultaneously pushing any of the aerosol that had accumulated within the duct into the pressure vessel.

The second method of heat application to the solid aerosol was from the same spark ignitor that was used for spark ignition of the agent/flammable gas mixture. The configuration was assembled as shown in Figure 2.13. As before, a specific quantity of aerosol was collected. It was then wrapped in cellophane and the pouch was sandwiched between the two igniter probes. In this configuration, the packet of aerosol chunks would completely burn and the igniter probes would then be available for checking the flammability of the mixture of aerosol and flammable gas that was later added.

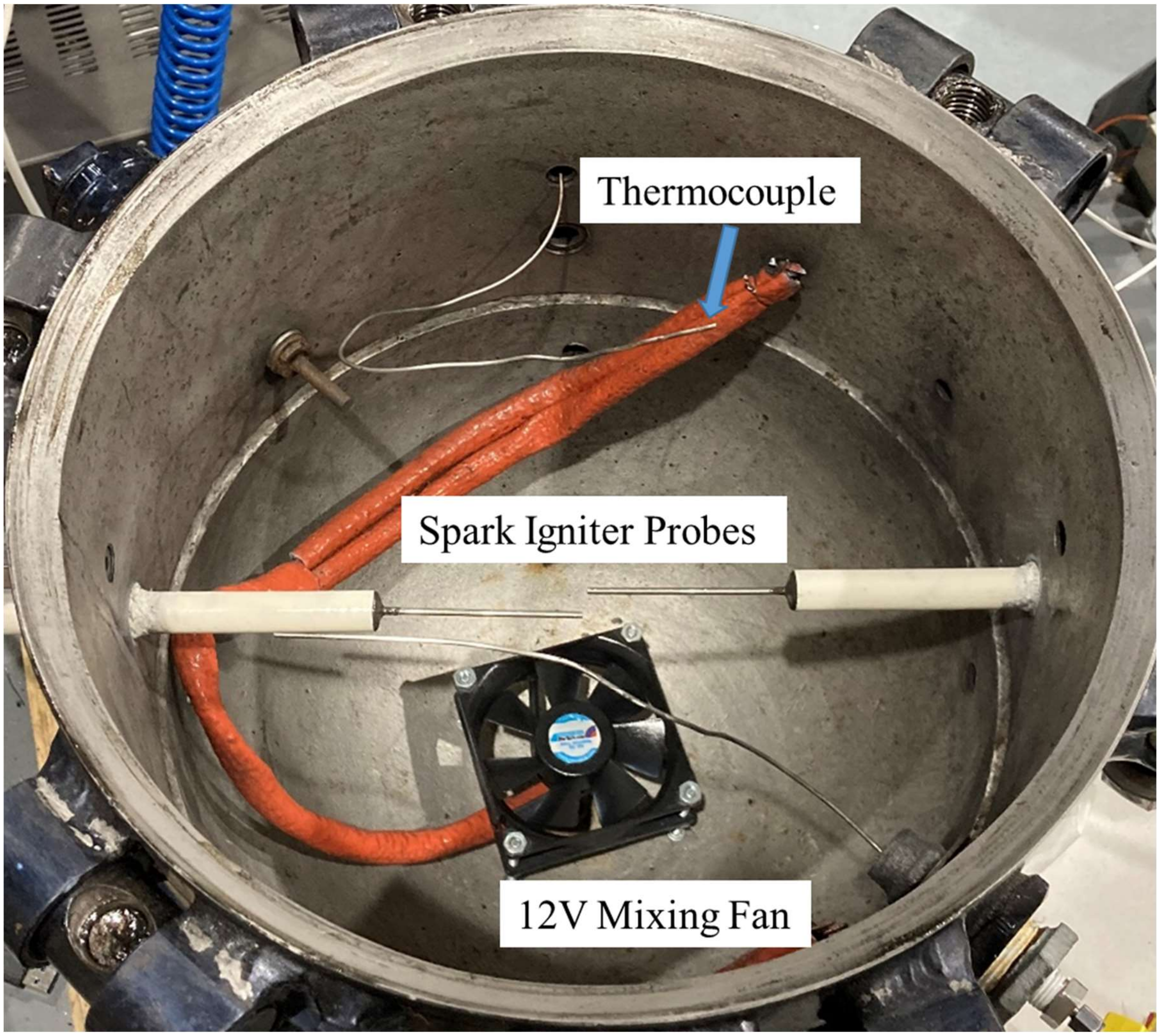


Figure 2.1: Pressure Vessel

Figure 2.2: 1mm RTV Layer on Piezo Electric Pressure Sensor

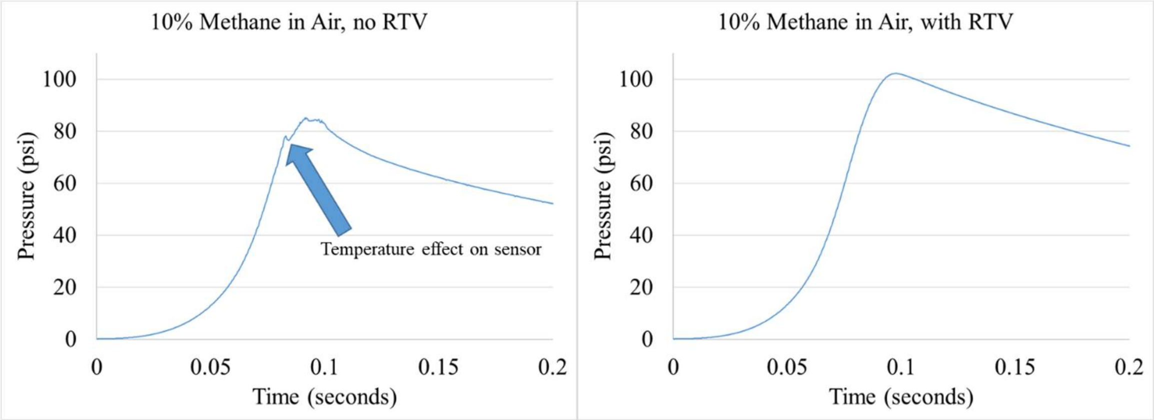


Figure 2.3: Effect of RTV on Pressure Sensor

Table 2.1: Purities of Gases used in this Study

| | |
|---|---|
| ***Air*** | Ultra Zero Grade |
| ***Hydrogen*** | 99.999% Purity |
| ***Methane*** | 99% Purity |
| ***Ethylene*** | 99.5% Purity |
| ***Carbon Monoxide*** | 99.5% Purity |
| ***Nitrogen*** | 99.999% Purity |
| ***Carbon Dioxide*** | 99.8% Purity |
| ***Halon 1301*** | Unknown Purity |
| ***2-BTP*** | Extracted from Handheld Extinguisher |
| ***Aerosol*** | A Solid that Creates an Aerosol Mixture when Activated |

Table 2.2: Gas Mixture used to Simulate Lithium Battery Vent Gases

| | |
|---|---|
| ***Hydrogen*** | 27.7% |
| ***Carbon Monoxide*** | 22.9% |
| ***Methane*** | 6.4% |
| ***Propylene*** | 4.52% |
| ***Ethylene*** | 2.19% |
| ***1-Butene*** | 1.58% |
| ***Ethane*** | 1.16% |
| ***Butane*** | .56% |
| ***Propane*** | .267% |
| ***Carbon Dioxide*** | 30% |
| ***Nitrogen*** | balance |

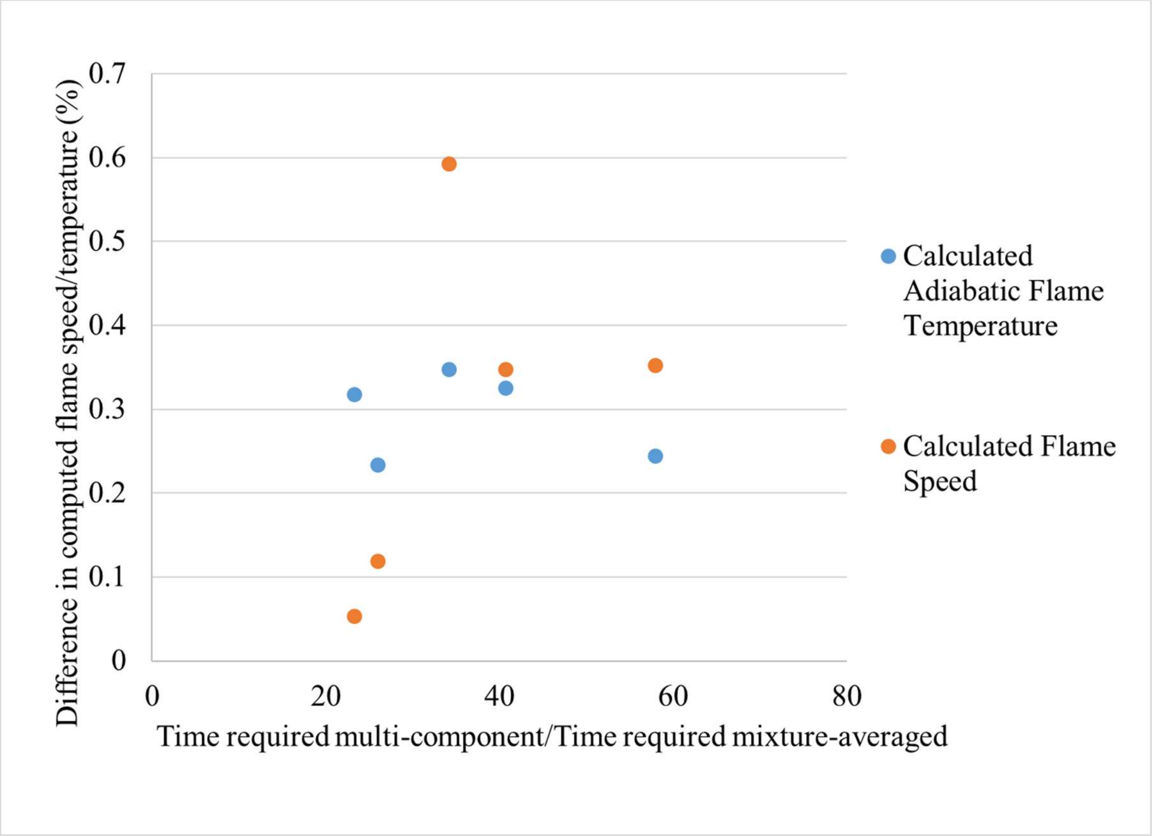


Figure 2.4: Comparison of Computational Time and Flame Speed for Multi-Component vs. Mixture Averaged Diffusion

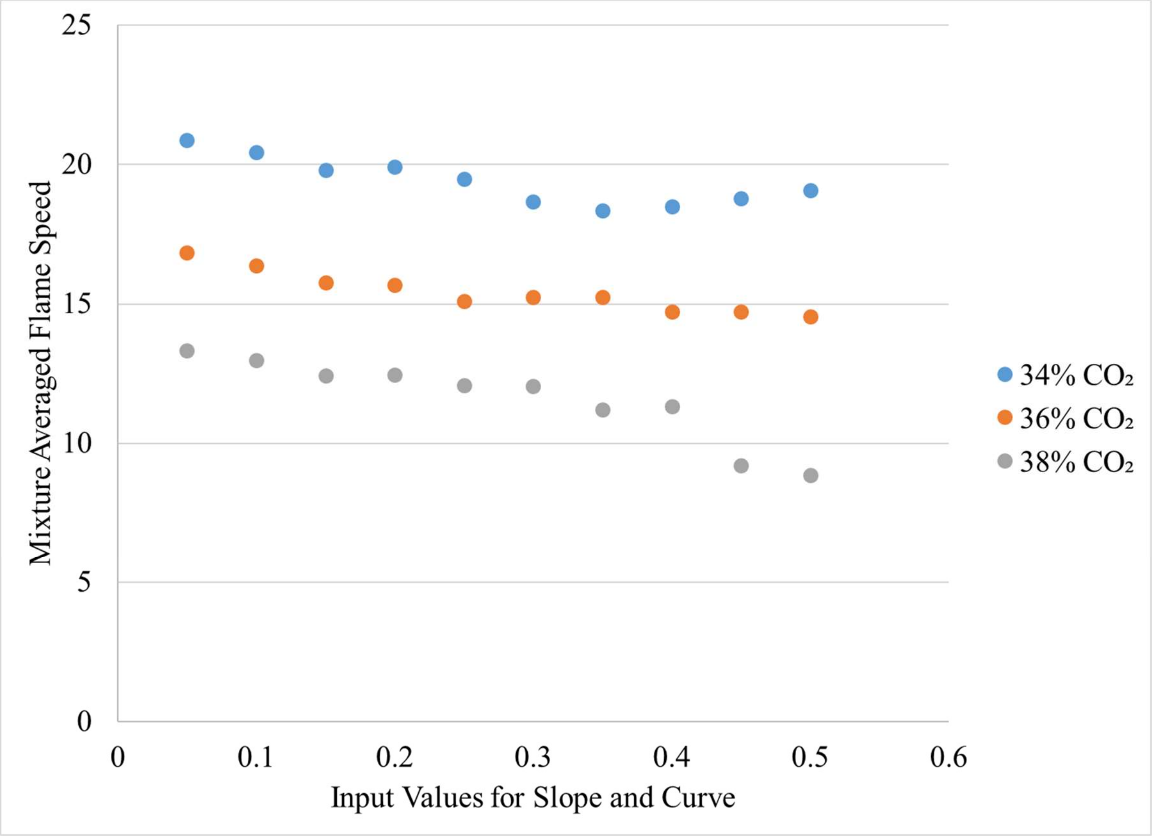


Figure 2.5: Calculated Flame Speed vs. Slope and Curve Values

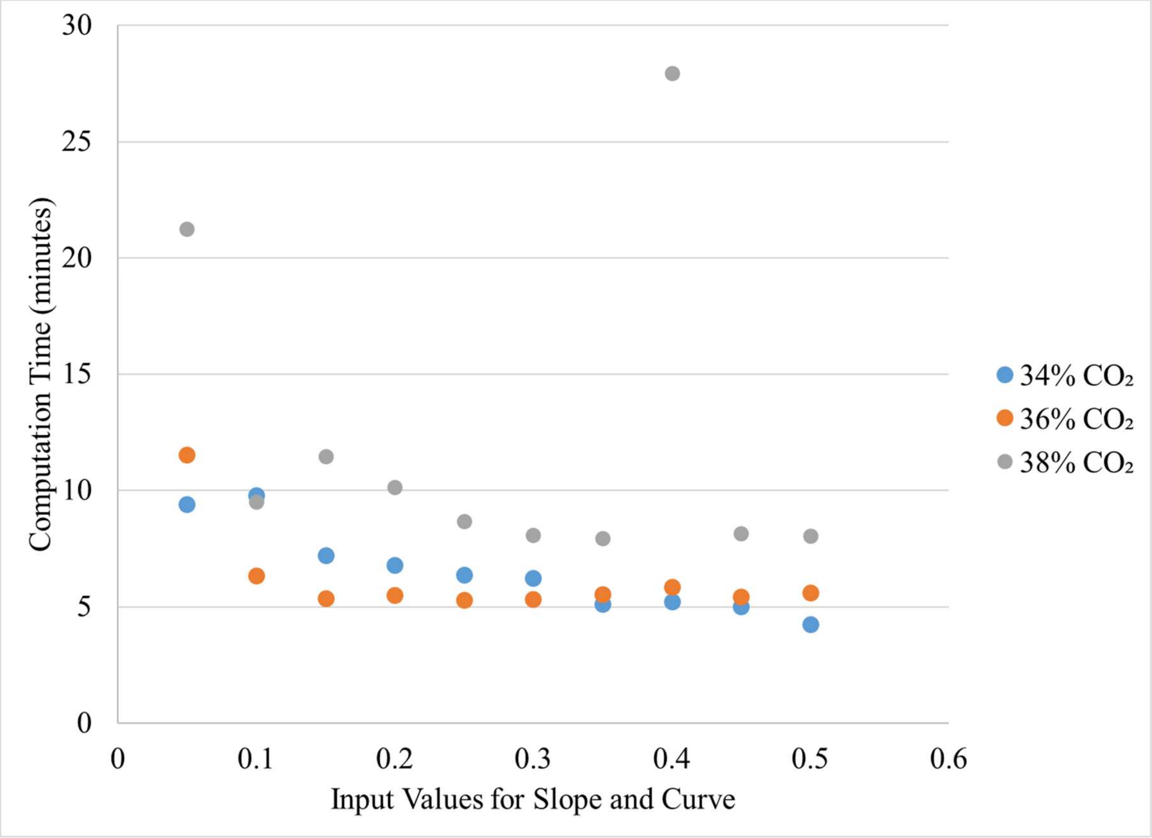


Figure 2.6: Computational Time vs. Slope and Curve Values

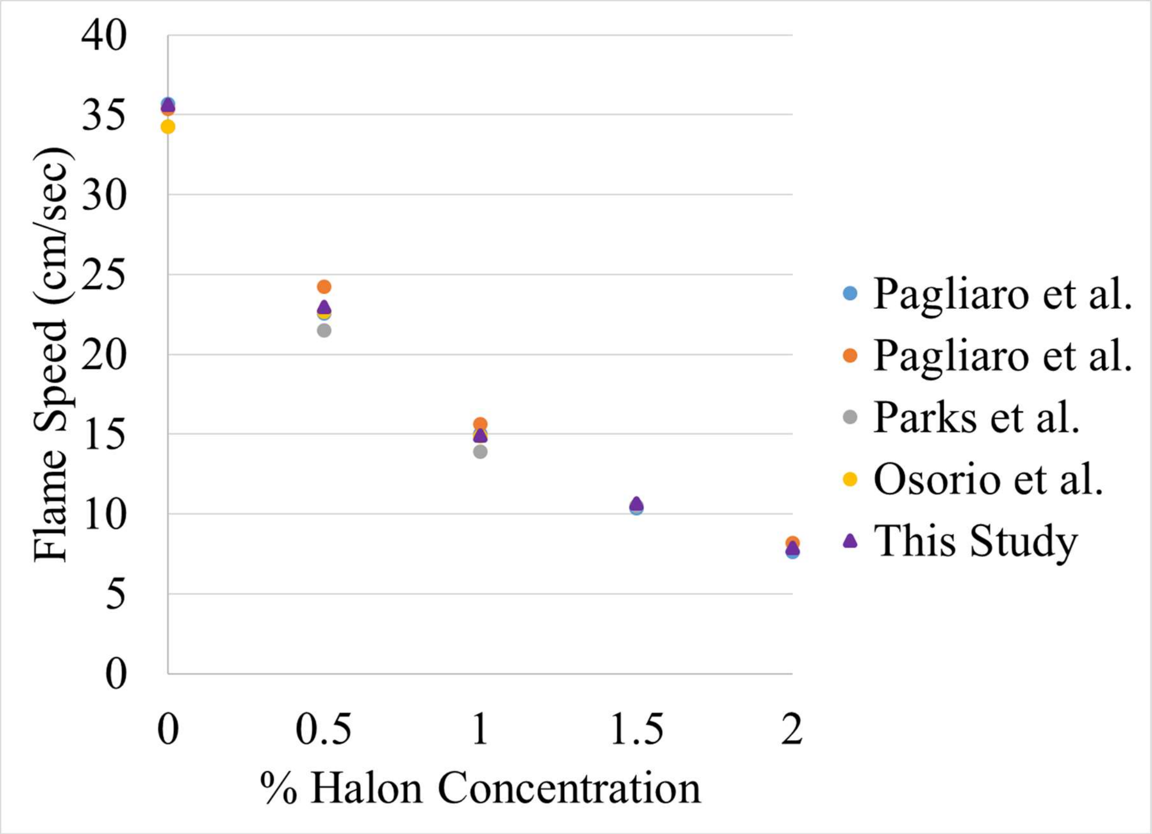


Figure 2.7: Simulated Flame Speed in this Study Compared to Literature, Pagliaro et al.: [52], Pagliaro et al.: [53], Parks et al.: [54], Osorio et al.: [55]

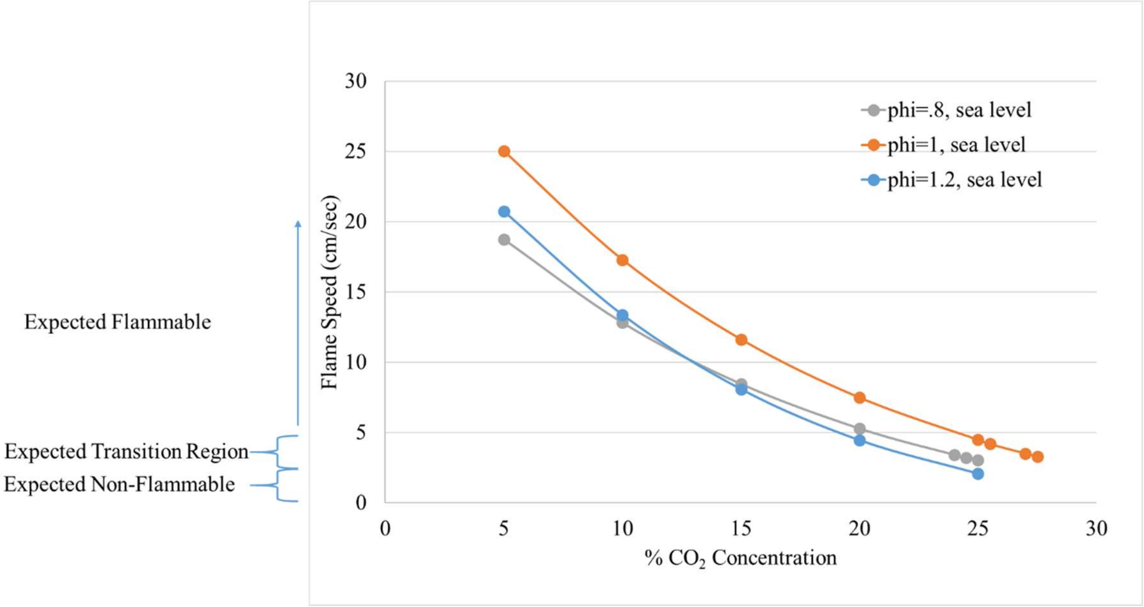


Figure 2.8: Methane and Carbon Dioxide Simulations

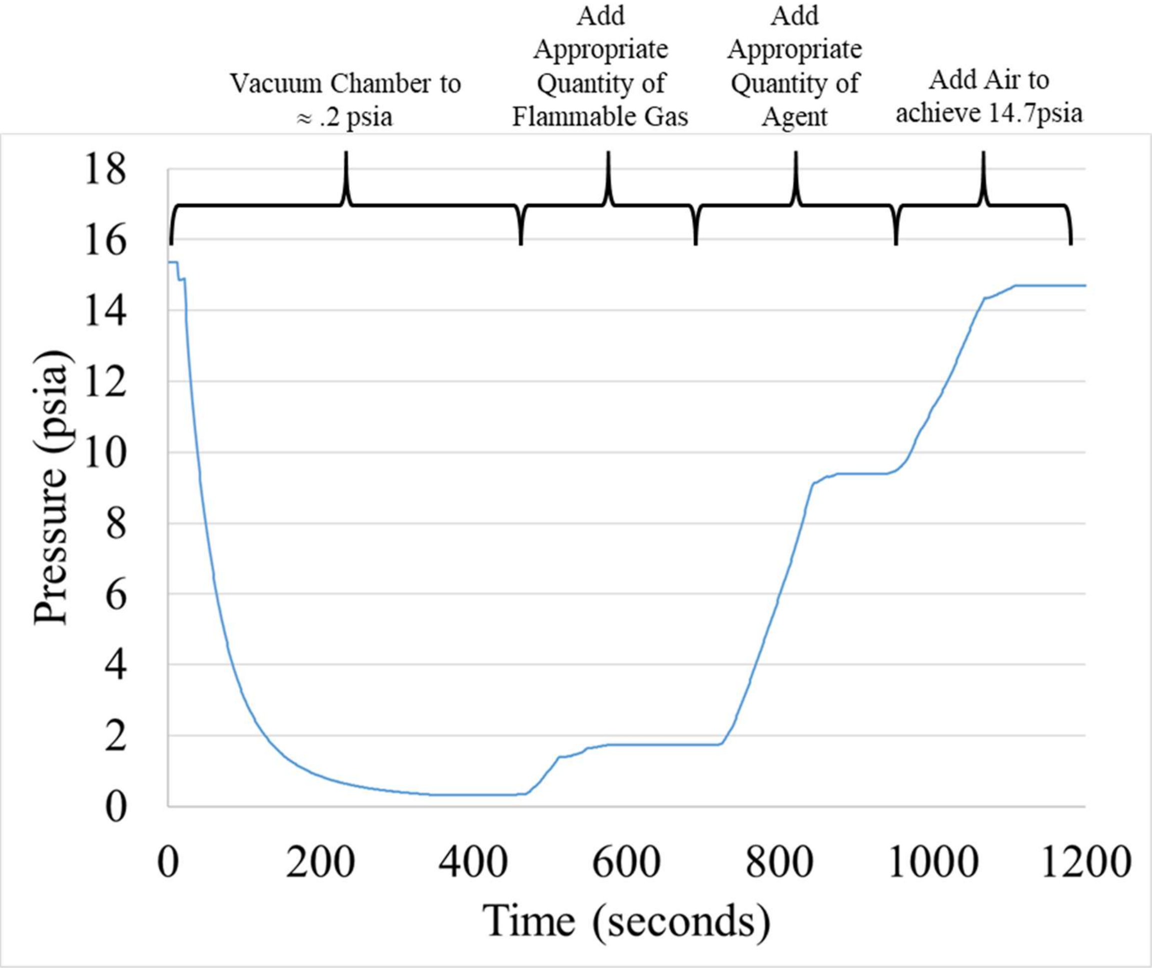
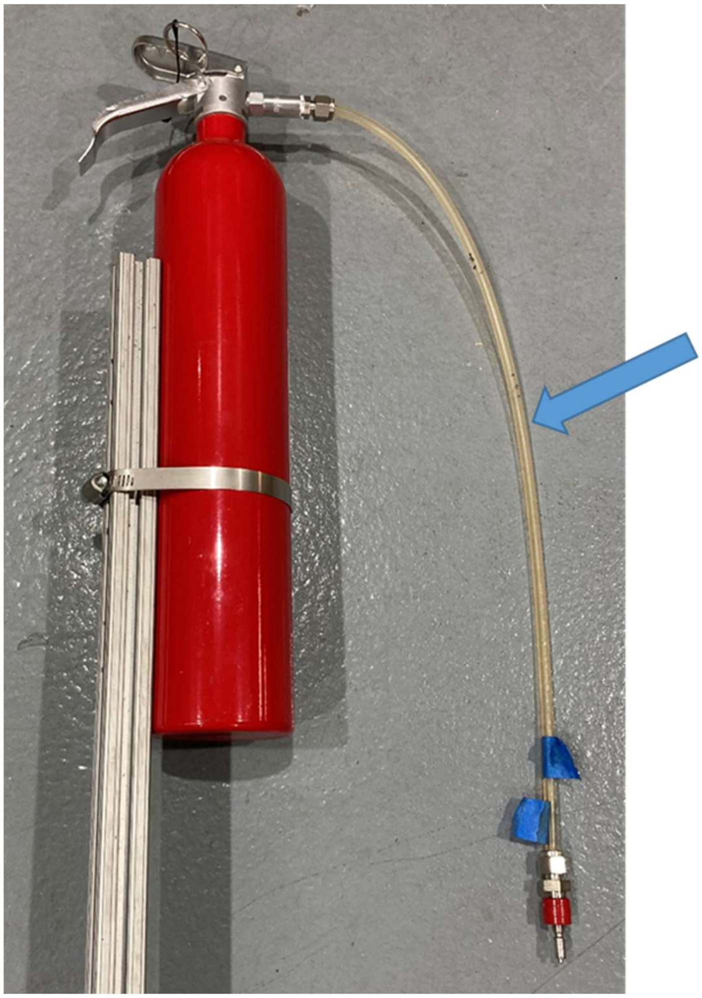


Figure 2.9: Example Test Sequence



2-BTP Volume Addition:
3.125 inches/mL

Figure 2.10: 2-BTP Addition Technique

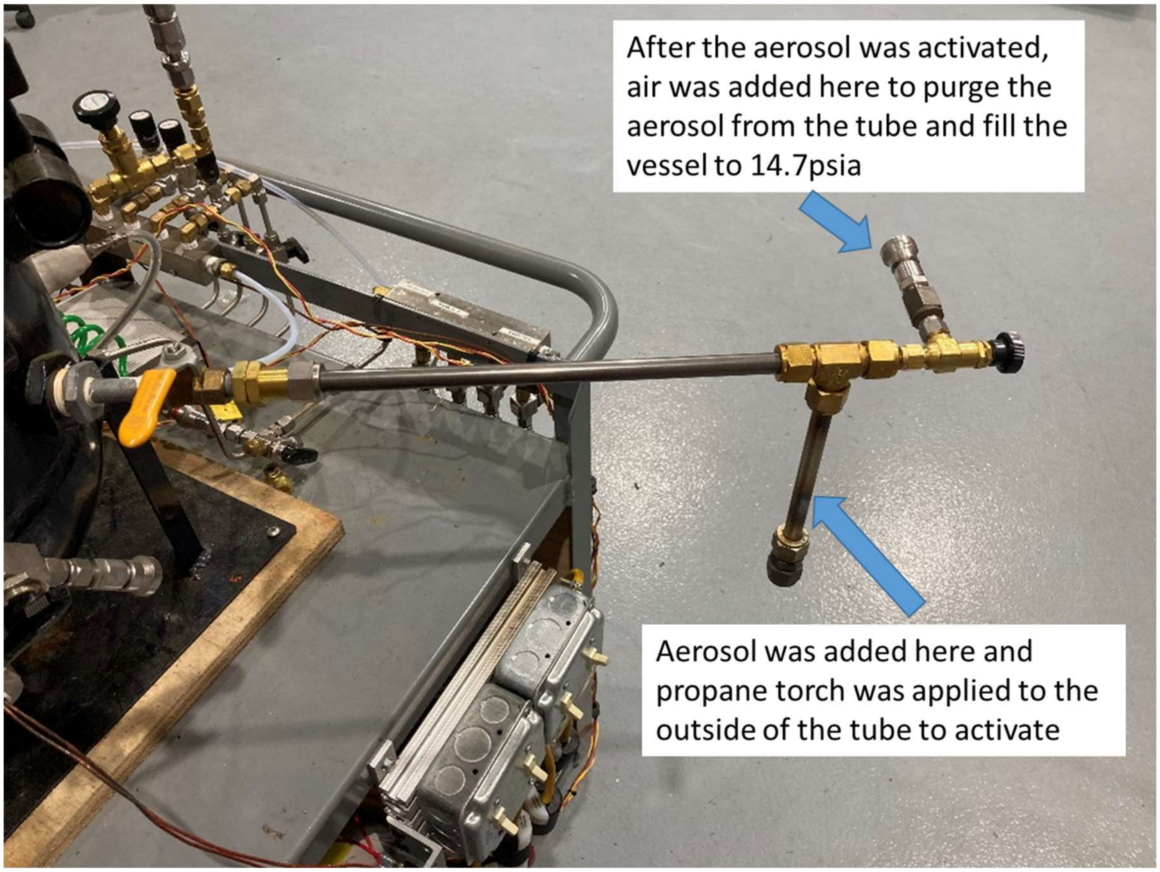


Figure 2.11: Initial Method of Aerosol Activation

Figure 2.12 Pre-Weighed Solid Aerosol Chunks Prior to Insertion into the Pressure Vessel

Figure 2.13: Final Method of Aerosol Activation. Aerosol was Sandwiched Within Cellophane Between the Igniter Probes.

# 3. Experiments

Tests were broken out into three sections. First, tests were performed with flammable gases at various flammable-gas/air concentrations to verify test setup functionality and consistency with literature. Once this was complete, a series of experiments were conducted with hydrogen and sub-inerting concentrations of Halon 1301 as well as hydrogen with sub-inerting concentrations of $CO_2$. Finally, a matrix of experiments were performed to find inerting concentrations of each of the extinguishing agents with each of the flammable gases. These later experiments were performed at equivalence ratios of 0.8 and 1.

## 3.1. Pressure rise bell-curves for flammable gases

Initial tests were performed to quantify pressure-rise vs. concentration for several flammable gases including methane and hydrogen as well as their rate-of-pressure-rise.

### 3.1.1. Procedure

The procedure for these initial tests was similar to the process described and shown in Figure 2.9 except extinguishing agents were not used. First, the vessel was vacuumed to 1 psia or less, as previously described. Next, flammable gases were added to the vessel to a predetermined pressure to give the desired concentration through the use of partial pressures. Finally, the bottled air was added to the vessel to bring the final pressure to 14.7 psia. The spark was then initiated and pressure data was recorded.

### 3.1.2. Results

These initial tests were performed to demonstrate that pressure rise profiles were repeatable and to compare results with what was available in literature. Figure 3.1 shows repeatability tests performed with methane. As shown in the figure, peak pressures were consistent from test-to-test. Maximum recorded pressures were 102.15psig, 101.04psig, and 100.7psig respectively and rise times were 0.097sec, 0.103sec, 0.102sec respectively.

At a hydrogen concentration of 30% by volume, a pressure rise of 101.94psig was achieved which was acceptably close to the results of Rehn [15] who achieved a pressure rise of 100.84 psig as given by Figure 3.2.

Several experiments were performed with hydrogen at various equivalence ratios. Rate-of-pressure-rise ($K_g$) was calculated from these results and compared to literature (Figure 3.3). As shown, results were consistent with the findings of other researchers and were most similar to the findings of Schroeder and Holtappels [7]. Their pressure vessel had a volume of 6 liters, which was relatively similar to the 21.15-liter vessel used in this study when considering the influence of vessel volume of $K_g$ as discussed previously in Section 1.2.1.

A series of experiments were also conducted to map-out a pressure vs. concentration bell curve for methane (Figure 3.4). As shown, hydrogen had a much wider flammability curve as expected. Peak pressure rise was roughly equal for both gases and occurred near an equivalence ratio of one.

## 3.2. Effect of sub-inerting Halon 1301 and $CO_2$ concentrations on flammable gases

Experiments were performed to investigate the behavior of Halon 1301 and $CO_2$ with hydrogen at sub-inerting concentrations. This provided insight into whether the addition of Halon 1301 agent was capable of causing an over-pressure event similar to what had been shown in literature with 2-BTP [26]. It also served to show a representative difference between two types of gaseous fire extinguishing agents. Halon 1301 was representative of an agent that reacted with intermediate radicals and $CO_2$ was representative of an inert gas that was considered non-reactive.

### 3.2.1. Procedure

In the second portion of this study, sub-inerting concentrations of extinguishing agents were mixed with flammable gases and the experimental procedure was carried out in a similar manner as previously described. The vessel was vacuumed to 1 psia or less. Flammable gases were then added to the vessel as required for the necessary concentration for that test. Bottled air was then added to bring the vessel pressure to 10 psia. Next, the appropriate quantity of extinguishing agent was added as quantified by pressure rise. Finally, bottled air was again added to bring the final pressure to 14.7 psia.

### 3.2.2. Results

Various tests were performed with Halon 1301 and $CO_2$ in an effort to observe their behavior with hydrogen at sub-inerting concentrations. At the required class-C aircraft cargo compartment knockdown concentration of 5%, Halon 1301 was unable to suppress hydrogen ignition. Further, Halon 1301 was also unable to suppress hydrogen ignition at 10% concentration (Figure 3.5).

At 20% and 25% $H_2$, the pressure rise was 83.88 psig and 100.11 psig respectively, which was greater than the pressure rise values of 80.1 psig (experimental) and 91 psig (experimental interpolated) that the pressures would have been without any Halon 1301. This demonstrated that the Halon 1301 was participating in exothermic reactions and therefore increasing the peak pressure, affirming that similar to 2-BTP, Halon 1301 can also experience overpressures.

With 10% Halon 1301, the pressure rise profile was significantly narrower compared to 5% Halon 1301. A peak pressure of 87 psig was observed at 25% $H_2$ which was below the pressure rise value of unsuppressed hydrogen combustion. This pressure rise was still far above what an aircraft cargo compartment could safely contain.

Results of tests conducted with carbon dioxide and hydrogen showed a decreasing flammability envelope as the carbon dioxide concentration increased. Hydrogen ignition was completely suppressed at a carbon dioxide concentration of 60%. Experiments conducted in the later part of this study (Section 3.3) specified the exact concentration required for carbon dioxide to suppress hydrogen for which the results were similar.

Although 5% Halon 1301 and 10% Halon 1301 did little to the peak pressure rise of combustion, rate-of-pressure-rise was significantly decreased as shown in Figure 3.6. This indicated that burning velocity was significantly slowed resulting in a significantly flatter $K_g$ profile. One explanation was that the exothermic reaction rate for the breakdown of Halon 1301 was much slower than hydrogen by itself. However, the exothermic heat release was still high enough to produce a significant pressure rise over time.

## 3.3. Determination of inerting concentrations of extinguishing agents on flammable gases

In the remaining set of experiments, tests were performed to find the inerting concentrations of various flammable gases. To compliment the experimental work and improve testing efficiency, simulations were conducted in parallel to experimentation.

### 3.3.1. Procedure

In the experimental procedure, flammable gases were added to achieve various equivalence ratios. Equivalence ratios were determined with the assumption that the extinguishing agents were non-reactive and reaction only occurred between the flammable gas and air. For example: 4% Halon 1301 with methane at phi=1 would have 4% Halon 1301, 9.12% methane and 86.88% air. In these tests, the inerting concentration was determined from interpolation of the pressure rise curve, as demonstrated in Figure 3.7.

The pressure rise criteria used to determine if a mixture was suppressed was 5%. For example, at atmospheric pressure, this corresponded to a pressure of:

$$14.7psia + .05 * 14.7psia = 15.435psia = .735\, psig$$

The increase of gauge pressure of .735psi at sea level was roughly the pressure required to dislodge the decompression panels in a Boeing 737 aircraft cargo compartment as previously discussed [4].

Simulations were performed with Cantera to evaluate the usefulness of laminar flame speed and adiabatic flame temperature at predicting gas mixture flammability. The simulations were also useful to advise the selection of initial concentrations to test in the pressure chamber experiments.

Tests and simulations were performed according to Table 3.1. As shown, the fire-extinguishing agents that were investigated were nitrogen, carbon dioxide, Halon 1301, a blend of 50% 2-BTP with 50% carbon dioxide by weight, and an aerosol. The flammable gases that were investigated were hydrogen, methane, ethylene, carbon monoxide and the battery gas mixture described in Section 2.2. These combinations of gases were also simulated in Cantera at various equivalence ratios (phi) and ambient conditions. 25000 feet was representative of the pressure in a depressurized aircraft cargo compartment and 200 degrees Celsius was representative of the temperature of a suppressed aircraft cargo compartment. In Table 3.1, each cell had a value of 0.8 or 1 representing the equivalence ratios that experiments or simulations or both were conducted.

### 3.3.2. Results

As shown in Table 3.2 and Table 3.3, Halon 1301 was extremely effective at suppressing CO ignition. This was likely related to the lack of hydrogen radicals to promote combustion. The 2-BTP/$CO_2$ ($C_3H_2F_3Br/CO_2$) mixture was significantly less effective against CO ignition. This was expected because, unlike Halon 1301, the 2-BTP/$CO_2$ mixture contained hydrogen molecules in its molecular structure. The results were consistent with a general understanding of the significant effect of $H_2O$ on combustion [56]. In most real-world scenarios, there will likely be a greater presence of water vapor in the reactants and this will likely decrease the effectiveness of Halon 1301 against CO. This was further supported by an opposite outcome of Halon 1301 with hydrogen combustion. Compared to other flammable gases, a significantly greater quantity of Halon 1301 was required with pure hydrogen.

It was interesting to note that both $N_2$ and $CO_2$ did not follow this same trend when reacting with CO even though they also did not have any hydrogen present. This was likely due to the principle by which each agent worked. As mentioned previously, inert gases like $N_2$ and $CO_2$ behave much differently than agents such as Halon 1301. Halon 1301 reacts and recombines with intermediate radicals. As mentioned, the presence of water vapor can significantly effect this process.

For all of the flammable gases, except for hydrogen, the greatest amount of Halon 1301 extinguishing agent was needed close to an equivalence ratio of 1. This was consistent with the assumption that the agent did not break down significantly with enough energy to behave as a fuel.

For hydrogen, 22.2% Halon 1301 was required for phi=1 but 25.13% was required for phi=.8. This indicated that Halon 1301 was reacting more exothermically with hydrogen than with other flammable gases. This was consistent with experiments described in Section 3.2 that showed an overpressure of certain concentrations of Halon 1301 and hydrogen.

Two considerations for fire extinguishing agents on aircraft were the required volume fraction of agent and the required mass fraction of agent. As shown in Table 3.2, a lesser volume of Halon 1301 was required than most other agents to suppress hydrogen ignition but a greater mass of Halon 1301 was required than any of the agents tested.

Similarly, when $CO_2$ and $N_2$ were used to suppress battery gas, at phi=1, 27.9% more $CO_2$ mass was required compared to $N_2$. However, 35.1% more $N_2$ than $CO_2$ was required by volume. This trend was the same for $CO_2$ and $N_2$ for all of the other flammable gases except methane, where a similar mass was needed for both $CO_2$ and $N_2$. At first glance, $N_2$ seemed more desirable for aircraft application because weight minimization is a significant driver in aircraft design. However, because a greater volume of $N_2$ was required compared to $CO_2$, $N_2$ will be more strongly effected by any leakage in the aircraft compartment. Preference for $CO_2$ or $N_2$ will depend on specific compartment design and application Figure 3.8 through Figure 3.12 help illustrate the difference between mass requirement and volume requirement for the extinguishing agents and flammable gases in this study.

Overall, Halon 1301 performed better than all other extinguishing agents for most of the flammable gases tested on a volume basis at phi=1. However, on a mass basis, 2-BTP/$CO_2$ performed better than all of the other agents, for all flammable gases except CO. As mentioned previously, Halon 1301 had exceptional performance against dry CO, but would likely lose part of that performance in real-life conditions where humidity was present.

A greater amount of 2-BTP/$CO_2$ was required at relatively lean mixtures than at stoichiometric mixtures for all flammable gases except CO. These results were in-line with a study done by Babushok et. al. that showed that 2-BTP would be less effective for lean methane flames because of an increase in heat release [33]. To investigate whether the peak in required inerting concentration occurred below an equivalence ratio of 0.8, an experiment was performed with methane and 2-BTP/$CO_2$ at an equivalence ratio of 0.6

(Table 3.4). Results showed that the equivalence ratio of .8 required a greater inerting concentration of 2-BTP/$CO_2$ than methane equivalence ratios of .6 and 1.

Nitrogen and Carbon Dioxide were shown to be 1.45% and 1.31% more effective by volume at suppressing lithium battery gas at sea level pressure than at aircraft cargo compartment altitude pressure. As shown in Table 3.2, 55.35% $N_2$ was required at 25k feet altitude whereas 53.9% $N_2$ was required at sea level pressure. Similarly, 41.2% $CO_2$ was required at 25k feet altitude and 39.89% $CO_2$ was required at sea level pressure.

When nitrogen/methane results were compared to literature, slightly more nitrogen was required in these experiments to create a "non-combustible" mixture. Literature results varied from 36.7% to 40.6% required $N_2$ but this study showed a slightly higher quantity of 43.6%. This was likely due to the method of flammability determination and, in particular, the amount of spark energy that was used in this study. The results of this study showed that 70.78% nitrogen was required to suppress hydrogen ignition and upward and downward flame propagation both required a 75% nitrogen concentration [50], [38]. Finally, literature showed that 50% nitrogen was required with ethylene [49] with downward flame propagation criteria and this study showed that 49.49% was required.

The inerting concentration for carbon dioxide in hydrogen of 55.23% was similar to the literature results of 56% that was found by Coward et al. in their experiment with downward flame propagation criteria but significantly different to their result of 61% found in their upward flame propagation test [36]. The inerting concentration of 27.36% carbon dioxide to suppress stoichiometric methane was similar to the results of [37] where they found a value of 28.59% using upward flame propagation criteria. Finally, inerting concentration for carbon dioxide and ethylene in this study was 43.76% and results from literature were 41% using downward flame propagation criteria.

Results with carbon monoxide were significantly different from some of the results found in literature. This study showed that a concentration of 37.62% carbon dioxide was required to inert carbon monoxide but [36] showed that 53% was required. Similarly, this study showed that 52.35% nitrogen was required to inert CO combustion but [36] showed that 68% was required. The difference was likely due to the method of assessing flammability as well as the potential presence of elevated humidity in their experiments.

The inerting concentration of 25.13% Halon 1301 at an equivalence ratio of .8 required to suppress hydrogen ignition was similar to literature results that ranged from 26.72% to 28.55%. This study showed that 5.98% Halon 1301 was required to suppress methane ignition, which was also similar to literature results that ranged from 6.145% to 7%. However, the quantity of 8.55% required to suppress ethylene combustion was different from the results of [48] that reported a required quantity of 12% Halon 1301 required. The flammability criteria of [48] was not known but would likely explain the difference of results.

Individual gas extinguishing agent inerting concentrations were examined to see if their combination could be used to predict the extinguishing agent inerting concentration of battery gas. Results followed a general weighted-average trend of the individual battery gas components if an assumption was made that all flammable hydrocarbon components other than methane had the same extinguishing agent inerting concentrations as ethylene. However, this calculation proved difficult because the battery gas came with its own concentration of 30% $CO_2$. The prediction for $CO_2$ was about 10% different from the actual value, the prediction for Halon 1301 was about .5% different from its actual value, $N_2$ was 14% different and 2-BTP/CO2 was 2.7% different. Therefore, for the agents tested, the four individual flammable gases would need a more complicated model than a simple weighted-average for the four flammable gases to be sole representative components of lithium battery gas.

## Aerosol Agent Results

As described in Section 3, the aerosol ignition tests were conducted in two different ways. The first method was by activating the aerosol with conductive heat provided from a torch and ducting it into the chamber. The second method was by activating it directly in the vessel with a spark. As shown in Figure 3.13, for the first method of activation, a significant quantity of aerosol was required for a relatively small increase in effectiveness.

Utilizing the second method of aerosol ignition provided much different results. When the aerosol was activated by the spark within the vessel, a quantity of 5 grams was sufficient to prevent stoichiometric (phi=1) methane ignition. However, when a second test was performed with the second method of ignition and 2.2 grams of aerosol, there was a pressure rise of 83.58psi.

A possible reason for the variation in results were that the aerosol was condensing or collecting within the tube during the first activation method. Whereas, when the aerosol was added directly to the vessel, there was no opportunity for any of the agent to be lost. More experiments beyond the scope of this study would be required to further explore these results.

## Prediction of Extinguishing Agent Inerting Concentrations from Laminar Flame Speed and Adiabatic Flame Temperature

Initially, simulations were run and compared to literature results to ensure the Python and Cantera configuration was set up properly. Results from these simulations were as shown in Figure 2.7. Flame speed results matched the results of literature at an acceptable level.

Once the model was validated with literature, flame speed simulations and adiabatic flame temperature simulations were run in Cantera for a variety of extinguishing agent concentrations with the selected flammable gases. Later, the simulations were evaluated to see if they could reasonably predict the inerting concentrations of extinguishing agents without the need to perform experiments to verify. Figure 3.14 through Figure 3.29 showed the simulation results for the various mixtures with the over-lay of experimentally found inerting concentrations. Additionally, Table 3.5 showed the inerting flame speeds for the various agent/flammable gas combinations at phi = 1, Table 3.6 showed the inerting adiabatic flame temperature for the various combinations at phi=1, Table 3.7 showed the inerting flame speed for the combinations at phi=.8 and Table 3.8 showed the inerting adiabatic flame temperature for the combinations at phi = 0.8.

The simulations proved to be an invaluable tool for picking initial extinguishing agent concentrations to perform experiments. Experiments took a lot of time and simulations were run overnight without any need of monitoring.

Overall, the estimation of agent inerting concentrations based on flame speed was acceptably accurate for methane at equivalence ratios of 0.8 and 1 and for ethylene at an equivalence ratio of 1. The behavior of hydrogen was slightly different. According to the model results, hydrogen was shown to be capable of sustaining a flame at a significantly reduced burning velocity of less than 1cm/sec. Interestingly, the inerting flame speed for hydrogen and carbon dioxide were very similar to the inerting flame speed for hydrogen and Halon 1301. This allowed the flammability for hydrogen mixtures to be predicted easily but with the assumption of a lower flame speed criteria.

Simulations showed that hydrogen inerting occurred at a relatively low adiabatic flame temperature whereas CO inerting occurred at a relatively high adiabatic flame temperature. Once again, once this was discovered, it was easier to predict inerting concentrations of other extinguishing agents before running tests.

For Halon 1301 with methane, ethylene, and battery gas, inerting adiabatic flame temperatures were around 2000K to 2100K. As mentioned previously, hydrogen and carbon monoxide behaved differently with inerting adiabatic flame temperatures around 1600K and 2350K respectively. It was interesting to note that battery gas behaved similarly to hydrocarbons (methane and ethylene) even though it was composed of a significant quantity of both hydrogen and carbon monoxide.

Unlike nitrogen and carbon dioxide, adiabatic flame temperature plots for Halon 1301 at phi=1 (Figure 3.22) were non-linear for all of the flammable gases. This gave a snapshot of the mechanisms for which Halon 1301 was operating. At different concentrations, various intermediate combustion species became increasingly more dominant in reaction profiles. This was likely due to Halon 1301 participating in the reactions and producing its own heat as was shown in Figure 3.5.

The mixture of 2-BTP/$CO_2$ also showed results that were different from the purely inert gases. As shown in Figure 3.24, for higher concentrations of agent, the profile began to trend concave-upwards. This was a possible indication that 2-BTP was reacting with the mixture at lower concentrations.

Similar to Halon 1301, mixtures of carbon dioxide with hydrogen showed an inerting adiabatic flame temperature below other gases. However, carbon monoxide and carbon dioxide inerting adiabatic flame temperatures were closer to the values of hydrocarbons. The inerting flame speed of most of the gases ranged between ~1400K to ~1650K with hydrogen at ~1100K.

Mixtures of 2-BTP/$CO_2$ with flammable gases showed all compositions to behave similarly. All of the inerting adiabatic flame temperatures occurred between ~1700K and ~1900K. The only outlier was methane. This once again pointed out the complexity with which reactions took place where differences in methane from other flammable gases increased its inerting adiabatic flame temperature by 200°C.

Inerting adiabatic flame temperature for nitrogen with other flammable gases was slightly more scattered than other agent/flammable gas mixtures similar to the behavior of carbon dioxide. As shown in Figure 3.25, hydrogen had the lowest adiabatic flame temperature of inertion and methane had the highest. The majority of mixtures had an inerting adiabatic flame temperature between ~1350K and ~1550K with hydrogen as an outlier at ~1000K.

## Effect of Increased Initial Ambient Temperature on Required Extinguishing Agent

Simulations were run to examine the effect that increased cargo compartment temperatures would have on required extinguishing agent inerting concentrations. In many aircraft fire scenarios, the ambient temperature of the cargo compartment for which extinguishing agent would be needed would be higher than 25°C. Therefore, it was important to know if the extinguishing agent would maintain its effectiveness.

Simulations were performed with Halon 1301 and battery gas at 200°C (Table 3.9, Table 3.10). A laminar flame speed of 1.55 cm/sec and an adiabatic flame temperature of 2021.5K were used as cutoff values for flame extinguishment as was previously determined at 25°C. Results showed that the predicted inerting concentration of Halon 1301 against battery gas using laminar flame speed as a metric was 13.87%. Using, adiabatic flame temperature as a metric, the Halon 1301 inerting concentration was 9.24%. In either case, a significantly greater quantity of Halon 1301 was required for elevated temperatures when compared to the requirement of 6.98% Halon 1301 at 25°C.

Similarly, additional estimated extinguishing agent inerting concentrations were determined for all other gas combinations utilizing flame speed and adiabatic flame temperature with the experimental results found at 25°C. Results were given by Table 3.9 and Table 3.10 respectively. As shown, using laminar flame speed to predict inerting concentrations tended to predict a higher required inerting concentration than predictions using adiabatic flame temperature. This highlighted the fact that these predictions should only be used as estimations to give a general sense for how agent/flammable gas combinations behave at elevated temperatures.

## Effect of Increased Altitude of Required Extinguishing Agent

Similar to temperature, it was necessary to understand the effect altitude had on the amount of extinguishing agent required. Simulations were run at 25000ft altitude to evaluate this effect. Additionally, two experiments were conducted with battery gas and nitrogen agent as well as battery gas with carbon dioxide agent to validate prediction.

The predicted inerting concentration for nitrogen and battery gas based on flame speed was 57.9% and the predicted inerting concentration based on adiabatic flame temperature was 53.77%. The actual inerting concentration based on experiment was 55.35%.

The predicted inerting concentration for carbon dioxide and battery gas based on flame speed was 44.03% and the predicted inerting concentration based on adiabatic flame temperature was 39.62%. The actual inerting concentration based on experiment was 41.2%.

In both cases, for nitrogen and carbon dioxide, the experimentally found inerting concentration fell between the predictions found from flame speed and adiabatic flame temperature.

As given in Table 3.11 and Table 3.12, when the predictions were applied to the other extinguishing agents, most of the results showed minimal difference between required inerting concentrations at 25k feet altitude vs. sea level. If anything, slightly more (< 5 %) agent was required at altitude than at sea level which was consistent with the results for nitrogen and carbon dioxide. For several of the mixtures, the simulations had trouble converging on a solution and no predictions were available.

## General Observations

When carbon monoxide was ignited with low concentrations of Halon 1301, blue ‘wispy’ flames were visible through a glass window in the top of the vessel. The flames sometimes propagated slowly throughout the vessel, creating a prolonged pressure-rise profile (Figure 3.30)

For other mixtures of gases, prolonged pressure-rise profiles were also observed. Ethylene with Halon 1301 at an equivalence ratio of .8 displayed a prolonged pressure-rise profile with two peaks. As the reaction was taking place, pressure and temperature slowly increased which enabled the reaction to progress further. The slower Halon 1301 decomposition reactions had time to speed up and the reaction was able to progress further.

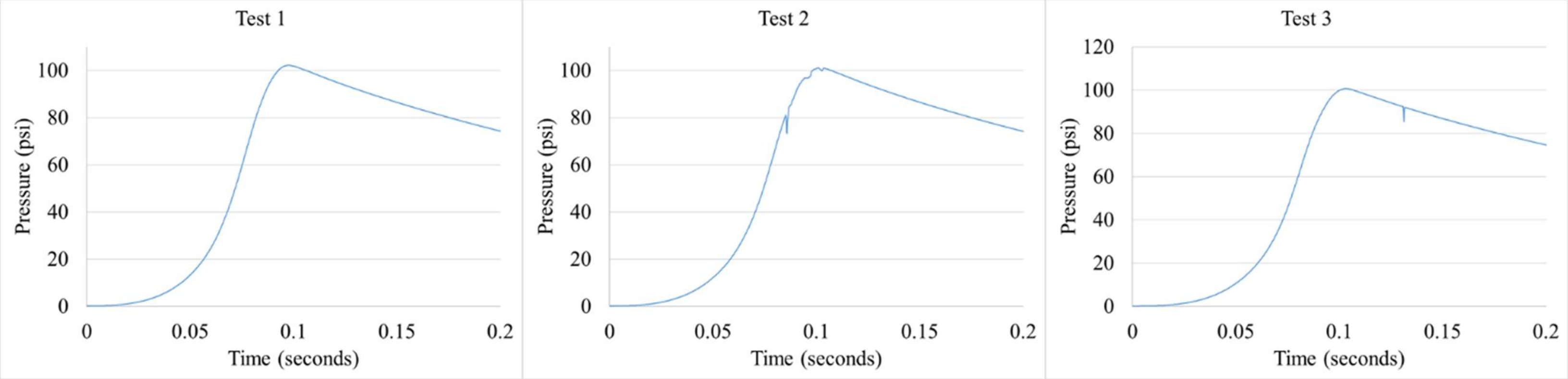


Figure 3.1: Methane (10% v/v) Repeatability

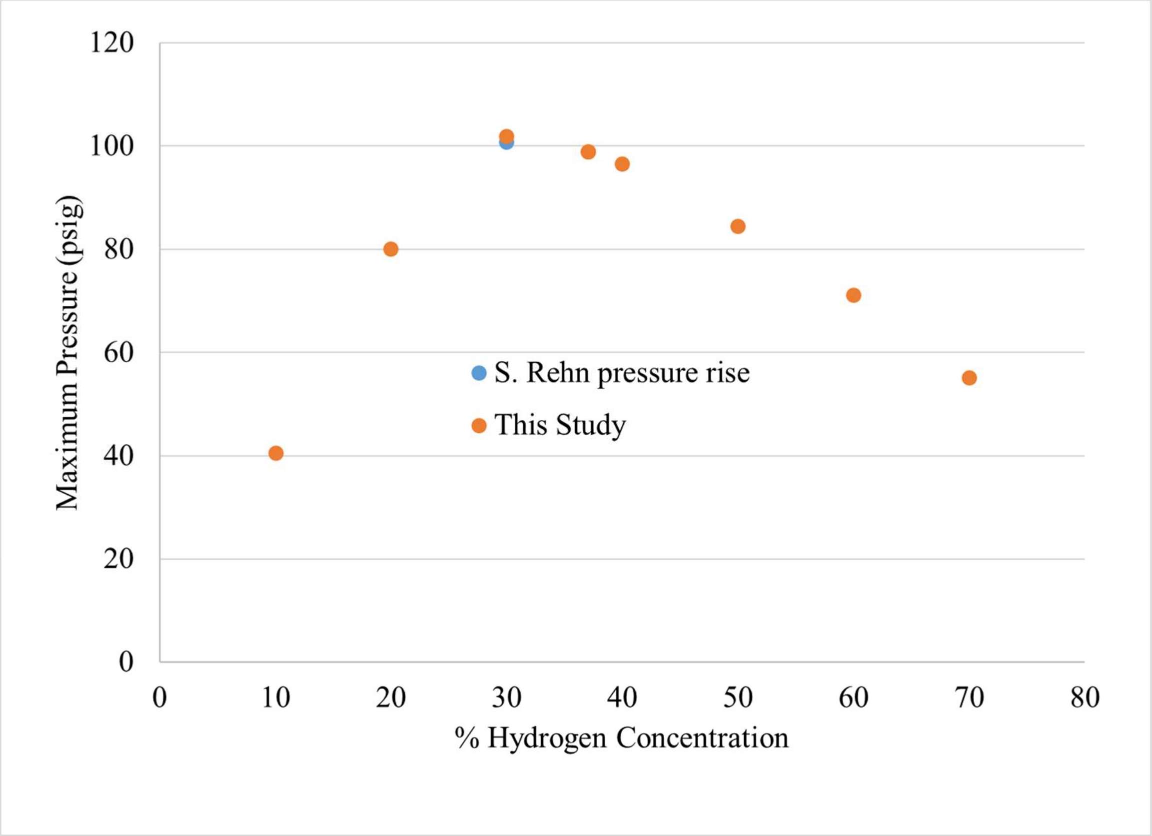


Figure 3.2: Comparison of Pressure Rise in this Setup Compared to Literature

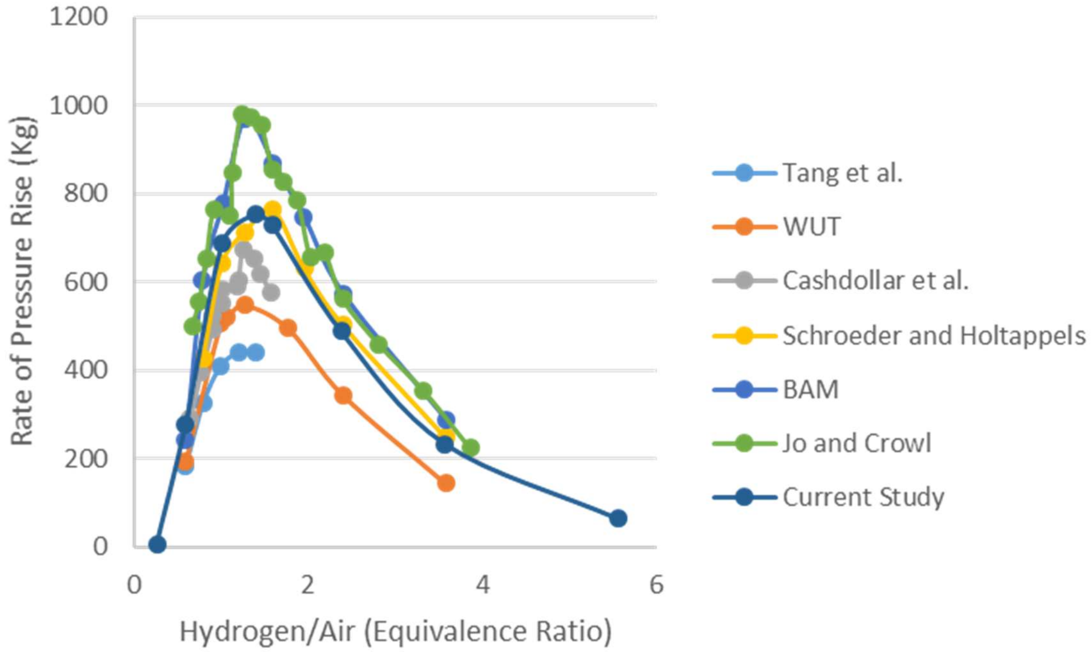


Figure 3.3: Comparison of Kg Values from this Study to Literature (Tang et al. [57], Warsaw University of Technology (WUT) [58], Cashdollar et al. [59], Schroeder and Holtappels [7], Federal Institute for Materials Research and Testing (BAM) [58], Jo and Crowl [60])

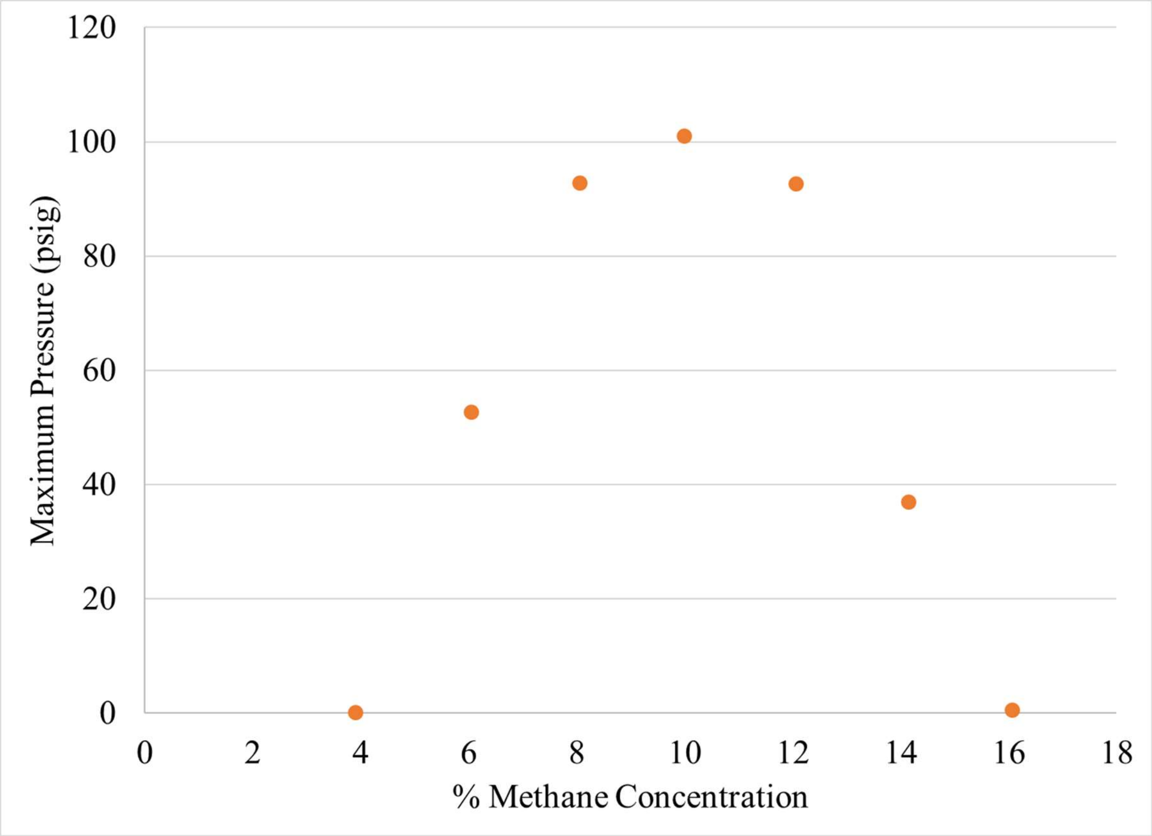


Figure 3.4 Pressure Rise from Methane Combustion vs. Concentration

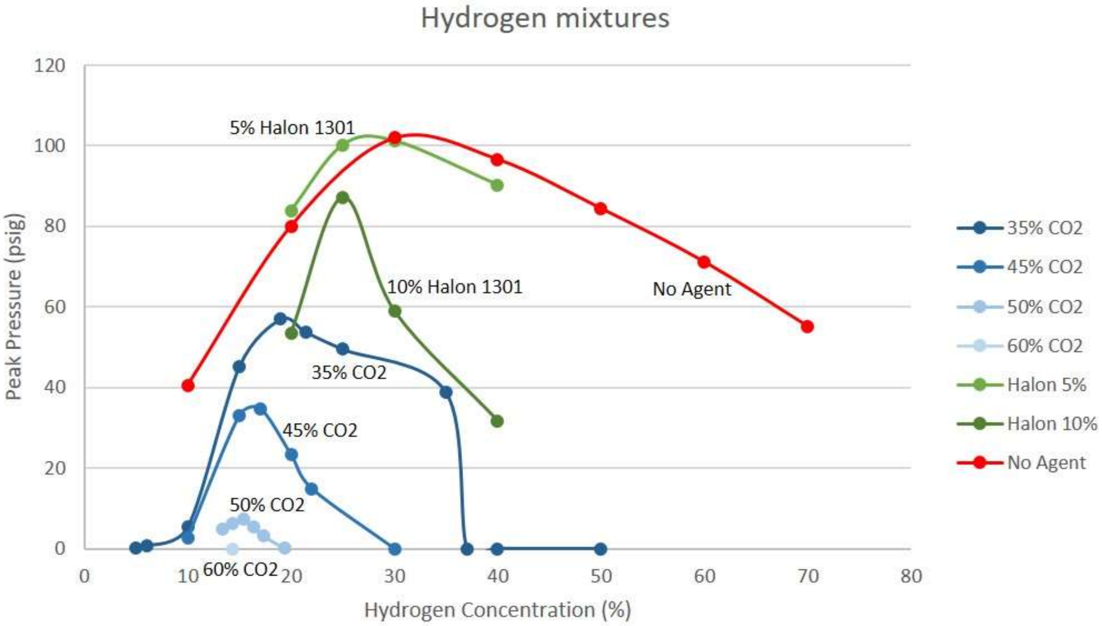


Figure 3.5: Pressure Rise Profiles for Various Concentrations of Halon 1301 and $CO_2$ with Hydrogen

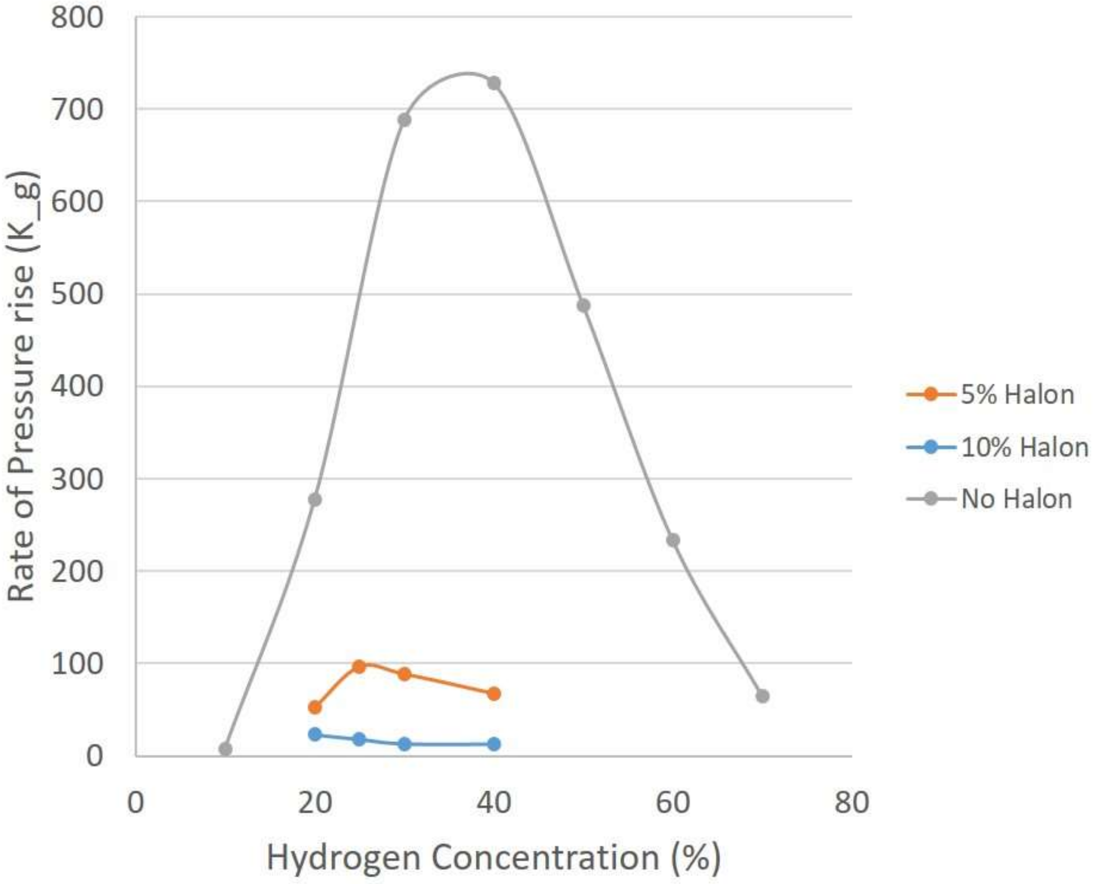


Figure 3.6: Rate-of-Pressure-Rise for Various Hydrogen/Halon 1301 Concentrations

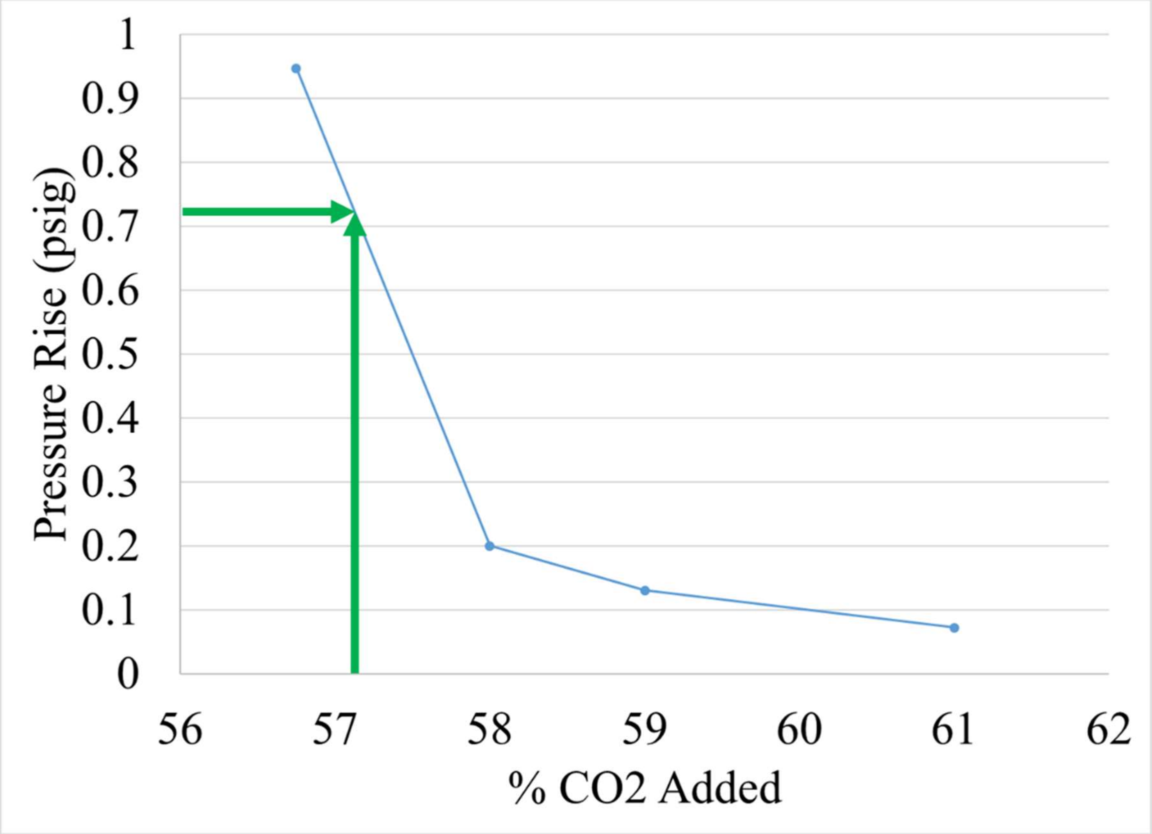


Figure 3.7: Interpolation Method used to Determine if a Mixture was Flammable

Table 3.1: Extinguishing Agent Inerting Concentrations - Tests Performed. Value in Each Cell Denotes Equivalence Ratio

| * Simulations and Experiments<br>** Experiments only<br>***Simulations only | **Nitrogen** | **Carbon Dioxide** | **Halon 1301** | **2-BTP/$CO_2$ Mix** | **Aerosol** |
|---|---|---|---|---|---|
| *Hydrogen* | .8*, 1* | .8*, 1* | .8*, 1* | .8*, 1* | n/a |
| *Methane* | .8*, 1* | .8*, 1* | .8*, 1* | .8*, 1* | 1** |
| *Ethylene* | .8*, 1* | .8*, 1* | .8*, 1* | .8*, 1* | n/a |
| *Carbon Monoxide* | .8*, 1* | .8*, 1* | .8*, 1* | .8*, 1* | n/a |
| *Battery Gases* | .8*, 1* | .8*, 1* | .8*, 1* | .8*, 1* | n/a |
| *Hydrogen, 200℃* | 1*** | 1*** | 1*** | 1*** | n/a |
| *Methane, 200℃* | 1*** | 1*** | 1*** | 1*** | n/a |
| *Ethylene, 200℃* | 1*** | 1*** | 1*** | 1*** | n/a |
| *Carbon Monoxide, 200℃* | 1*** | 1*** | 1*** | 1*** | n/a |
| *Battery Gases, 200℃* | 1*** | 1*** | 1*** | 1*** | n/a |
| *Hydrogen, 25k feet altitude* | n/a | n/a | 1*** | 1*** | n/a |
| *Methane, 25k feet altitude* | 1*** | 1*** | 1*** | 1*** | n/a |
| *Ethylene, 25k feet altitude* | 1*** | 1*** | 1*** | 1*** | n/a |
| *Carbon Monoxide, 25k feet altitude* | 1*** | 1*** | n/a | n/a | n/a |
| *Battery Gases, 25k feet altitude* | 1* | 1* | n/a | 1*** | n/a |

Table 3.2: Experimental Results, phi=1

| ***Experimental results, phi = 1*** | **Nitrogen Required** | **Carbon Dioxide Required** | **Halon 1301 Required** | **2-BTP/$CO_2$ Mix Required** |
|---|---|---|---|---|
| *Hydrogen* | 69.45 %<br>16.6 grams | 55.23 %<br>22.9 grams | 22.2 %<br>28.6 grams | 17.37 %<br>11.04 grams |
| *Methane* | 43.6 %<br>10.4 grams | 27.36 %<br>11.3 grams | 5.98 %<br>7.7 grams | 9.42 %<br>5.83 grams |
| *Ethylene* | 57.27 %<br>13.7 grams | 43.76 %<br>18.1 grams | 8.55 %<br>11 grams | 17.43 %<br>10.94 grams |
| *Carbon Monoxide* | 52.35 %<br>12.5 grams | 37.62 %<br>15.6 grams | .264 %<br>.34 grams | 15.67 %<br>9.78 grams |
| *Battery Gases* | 53.9 %<br>12.9 grams | 39.89 %<br>16.5 grams | 6.98 %<br>9 grams | 13.45 %<br>8.39 grams |
| *Battery Gases 25k feet* | 55.35 %<br>13.3 grams | 41.2 %<br>17.1 grams | n/a | n/a |

Table 3.3: Experimental Results, phi=.8

| ***Experimental results, phi = .8*** | **Nitrogen Required** | **Carbon Dioxide Required** | **Halon 1301 Required** | **2-BTP/$CO_2$ Required** |
|---|---|---|---|---|
| *Hydrogen* | 70.78 %<br>16.95 grams | 56.67 %<br>23.5 grams | 25.13 %<br>32.35 grams | 19.62 %<br>12.35 grams |
| *Methane* | 37.65 %<br>9.02 grams | 24.92 %<br>10.33 grams | 3.98 %<br>5.12 grams | 11.39 %<br>7.16 grams |
| *Ethylene* | 49.49 %<br>11.85 grams | 35.83 %<br>14.86 grams | 4.78 %<br>6.15 grams | 19.37 %<br>12.28 grams |
| *Carbon Monoxide* | 45.56 %<br>10.9 grams | 31.69 %<br>13.14 grams | 0.24 %<br>0.31 grams | 12.08 %<br>7.57 grams |
| *Battery Gases* | 49.77 %<br>11.92 grams | 36.63 %<br>15.19 grams | 6.06 %<br>7.8 grams | 16.67 %<br>10.41 grams |

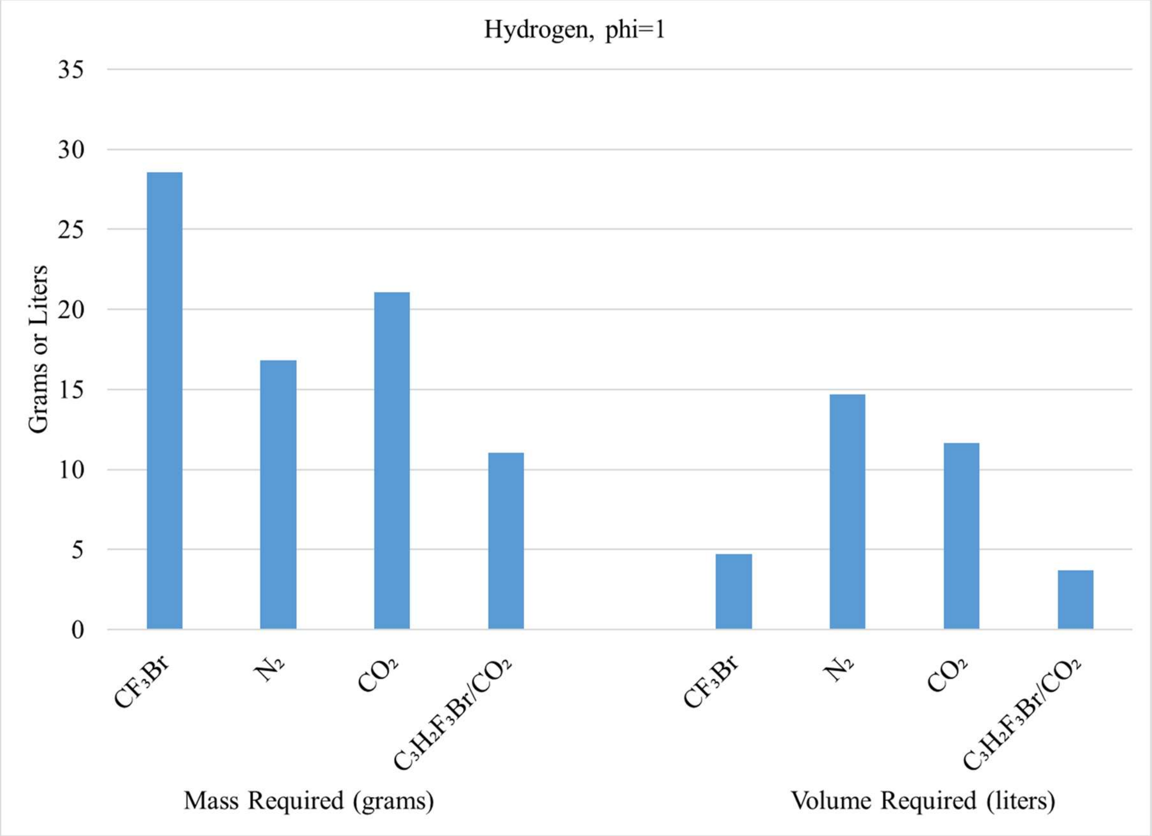


Figure 3.8: Quantity of Extinguishing Agent Required to Inert Hydrogen

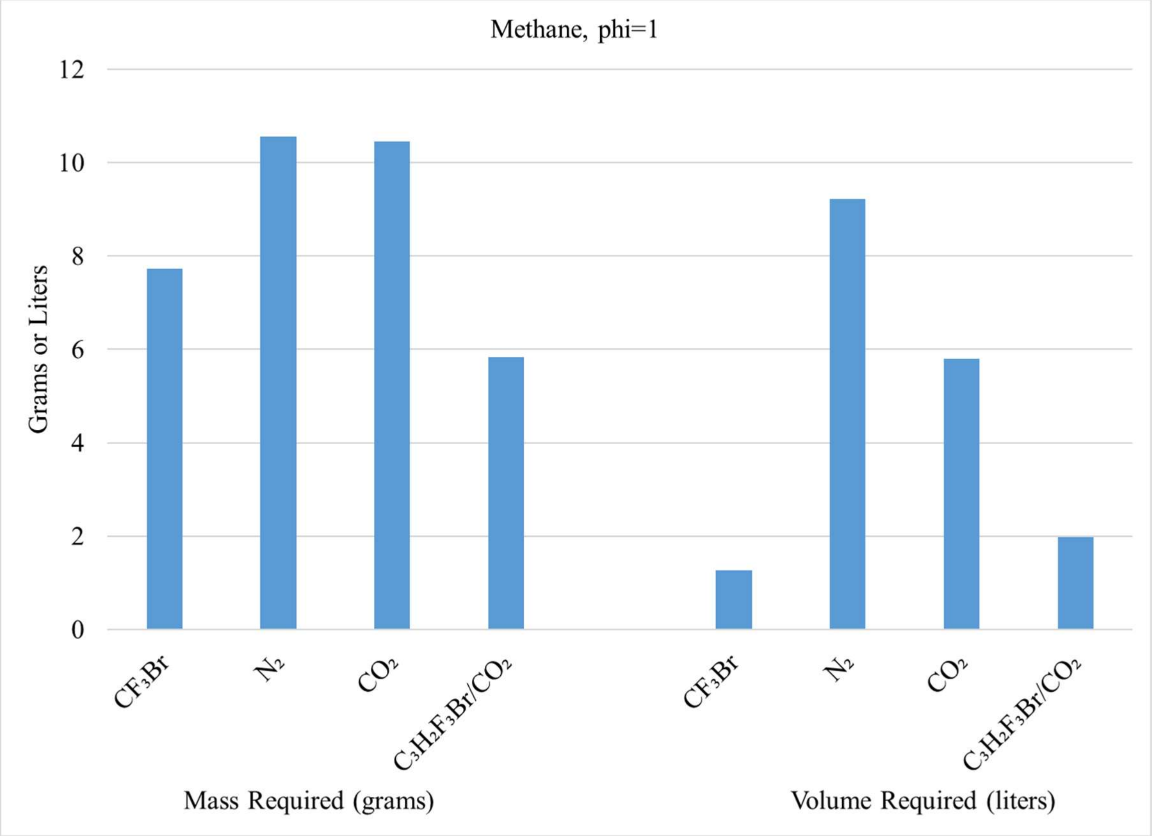


Figure 3.9: Quantity of Extinguishing Agent Required to Inert Methane

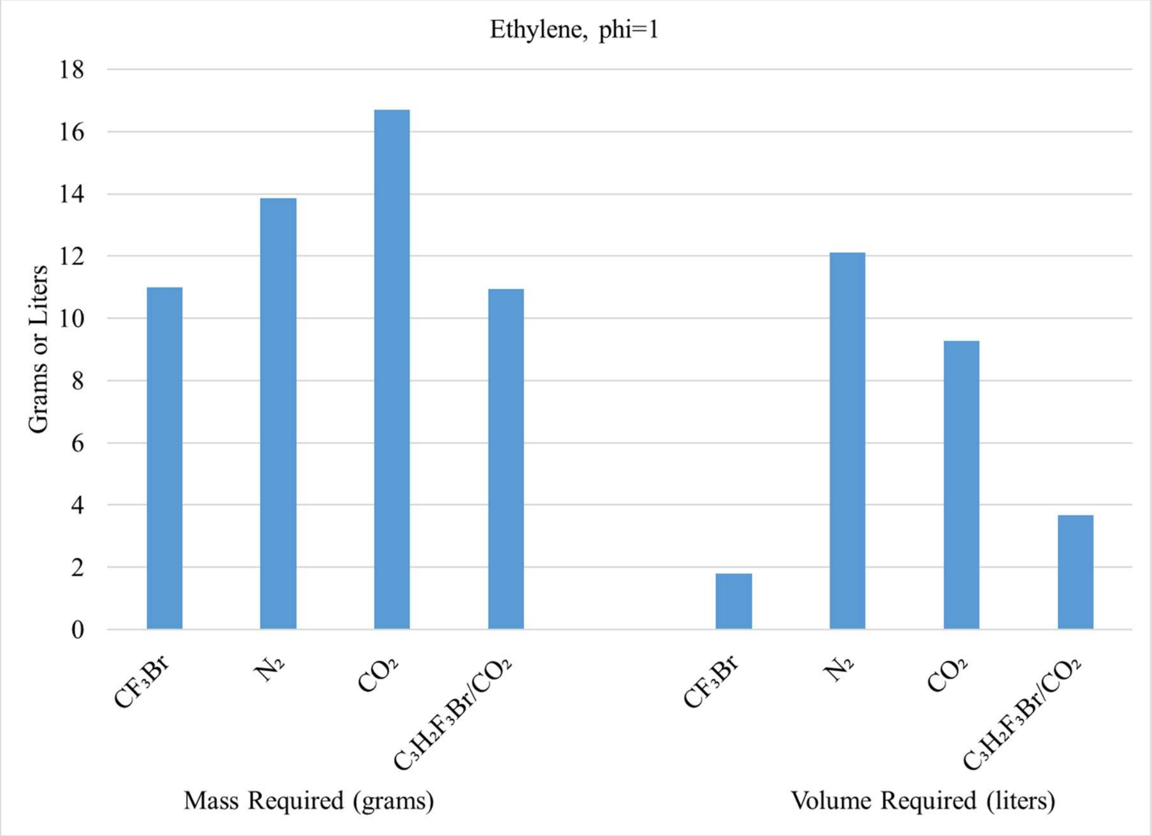


Figure 3.10: Quantity of Extinguishing Agent Required to Inert Ethylene

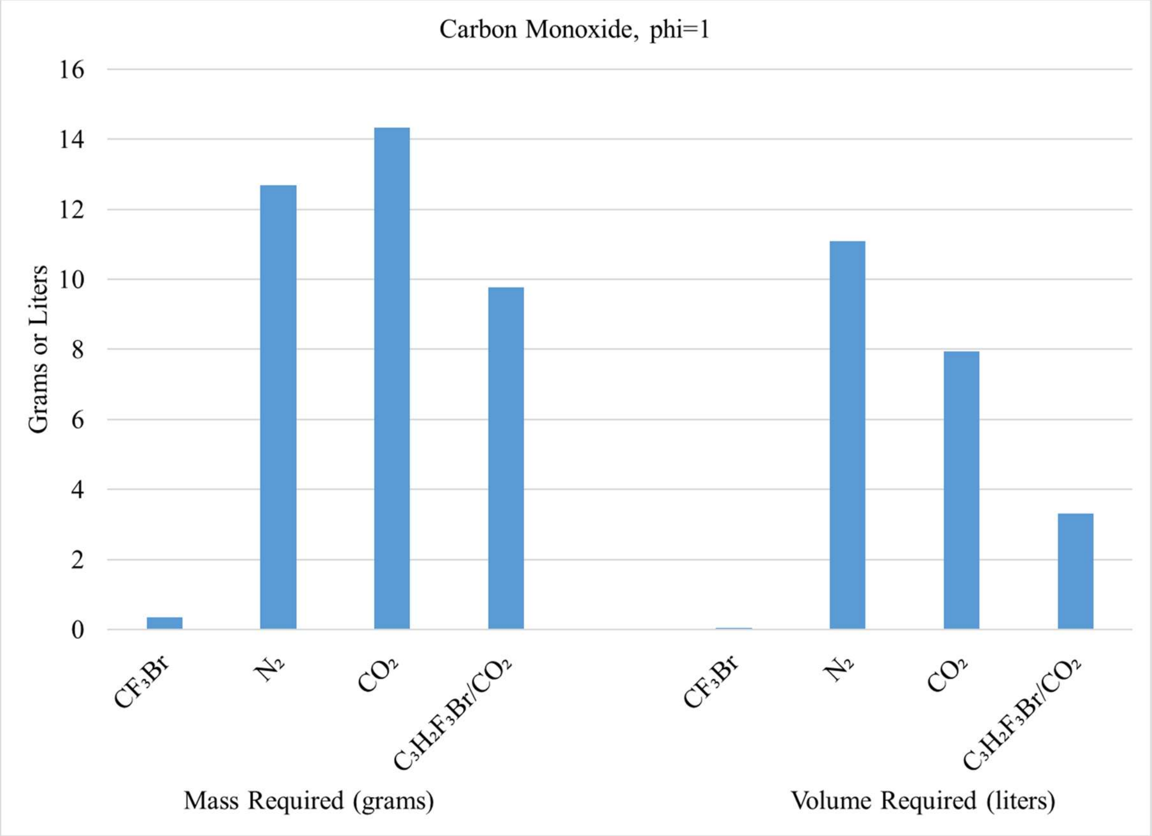


Figure 3.11: Quantity of Extinguishing Agent Required to Inert Carbon Monoxide

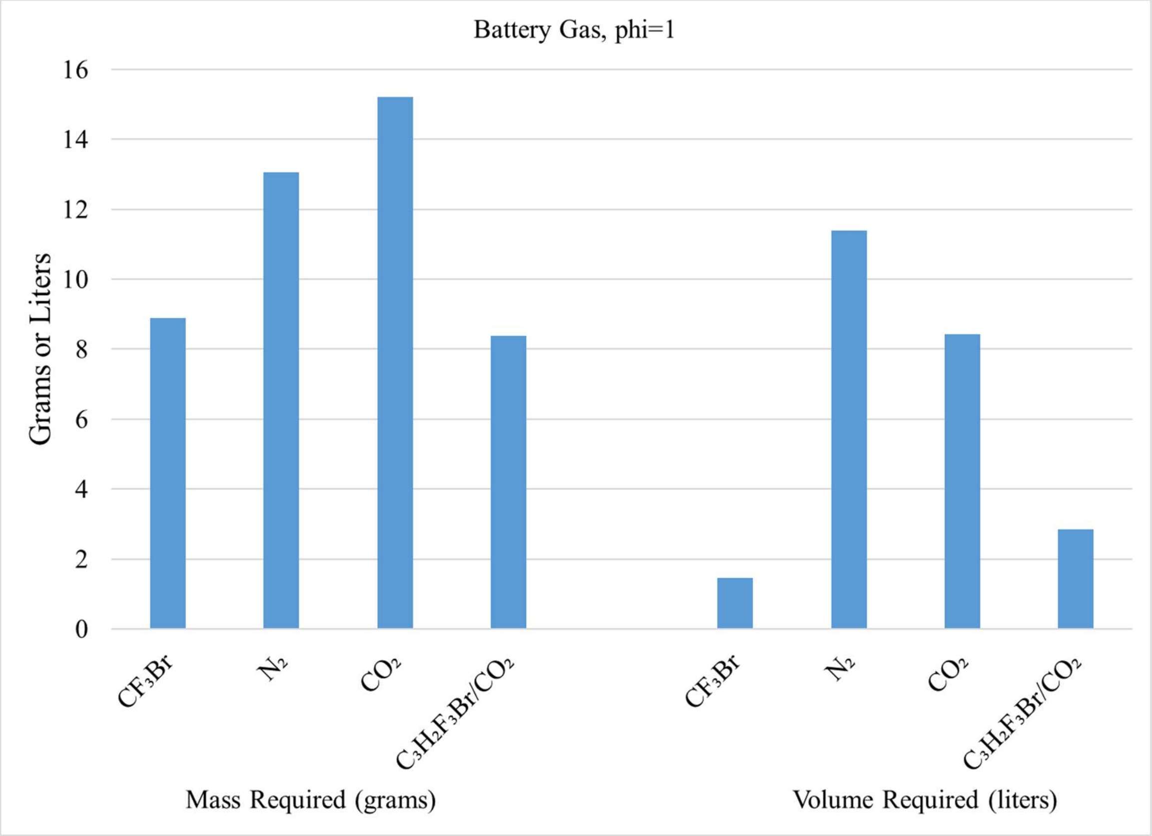


Figure 3.12: Quantity of Extinguishing Agent Required to Inert Battery Gas

Table 3.4: Experimental Results, phi=.6

| ***Experimental results, phi = .6*** | **Nitrogen** | **Carbon Dioxide** | **Halon 1301** | **2-BTP/$CO_2$ Mix Required** |
|---|---|---|---|---|
| *Methane* | n/a | n/a | n/a | 6.79 %<br>4.23 grams |

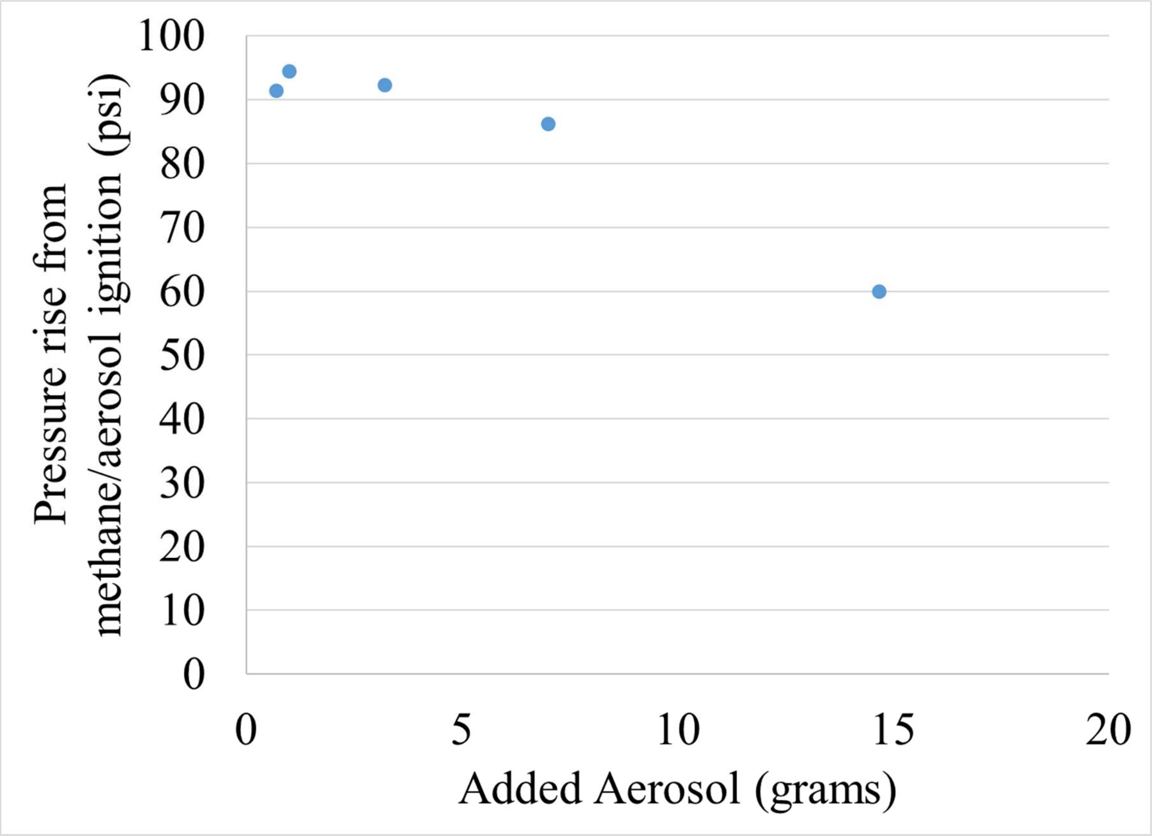


Figure 3.13: Pressure Rise from Ignition of Methane with Varied Quantities of Aerosol; External ignition of Aerosol

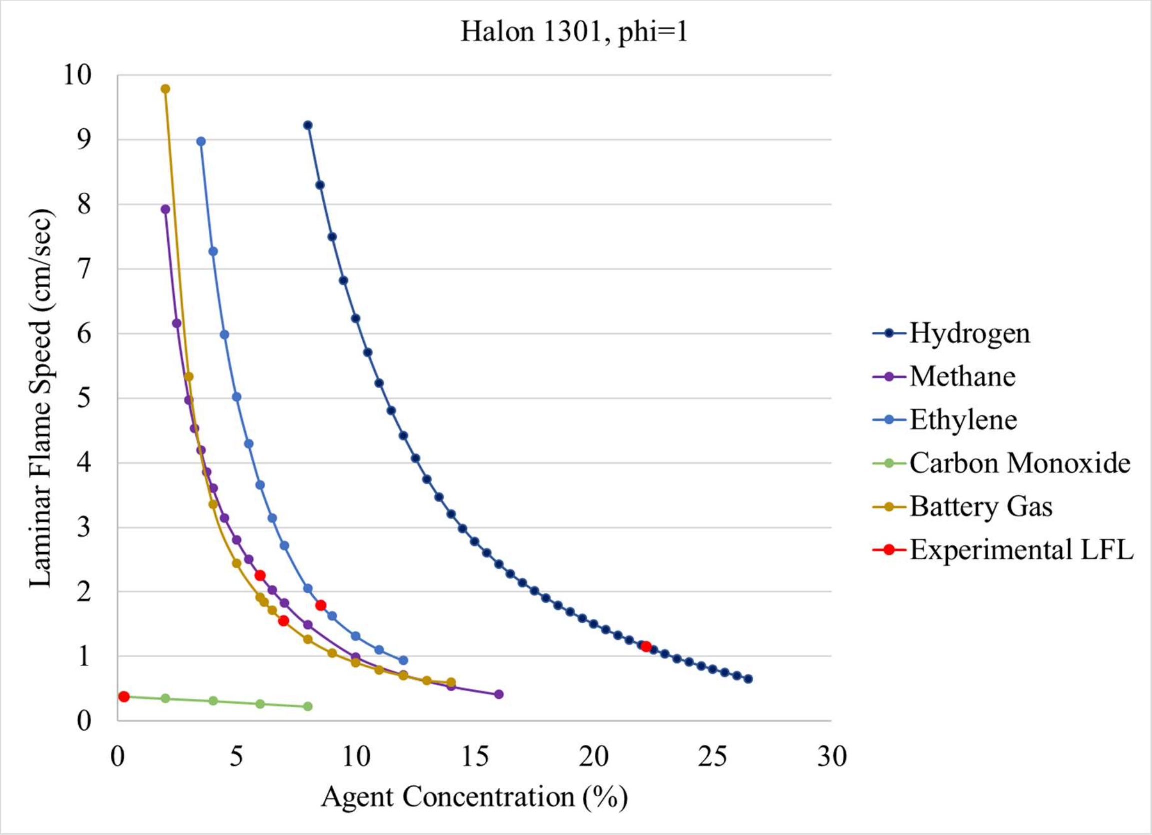


Figure 3.14: Variation of Laminar Flame Speed with Concentration of Halon 1301, phi=1

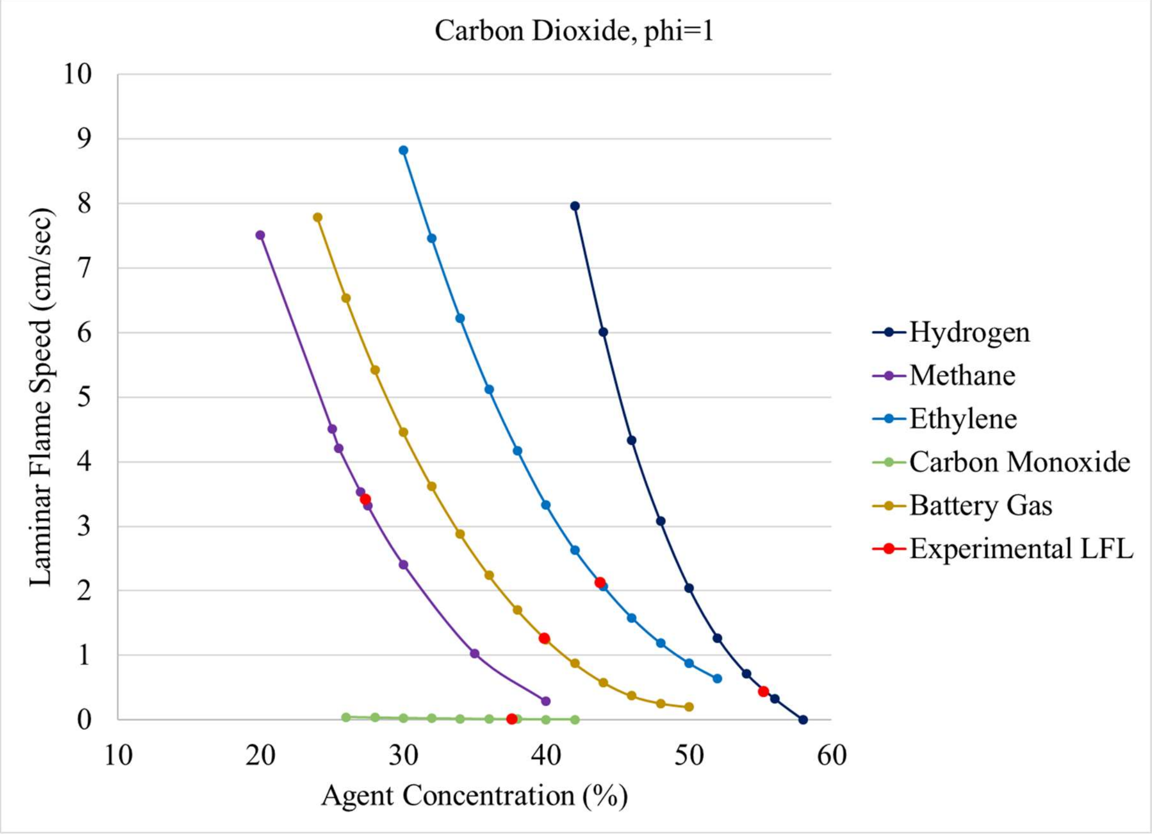


Figure 3.15: Variation of Laminar Flame Speed with Concentration of Carbon Dioxide, phi=1

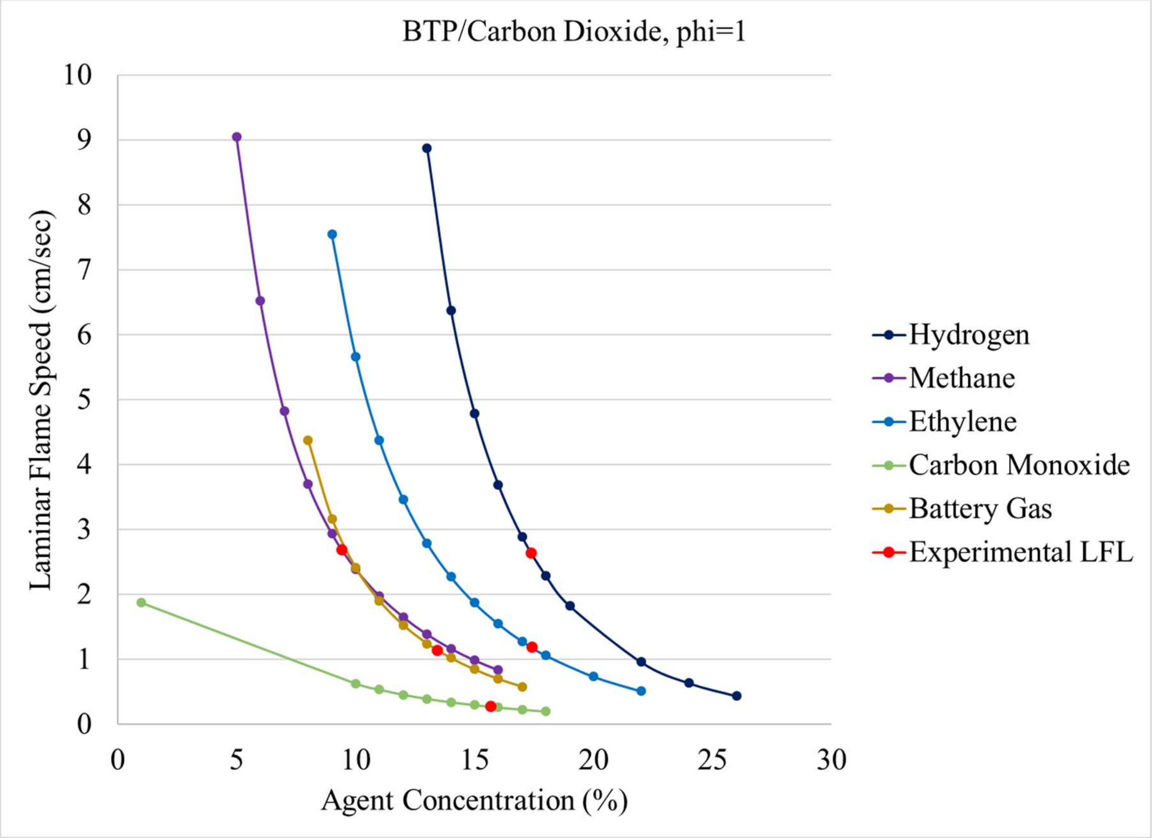


Figure 3.16: Variation of Laminar Flame Speed with Concentration of 2-BTP/Carbon Dioxide, phi=1

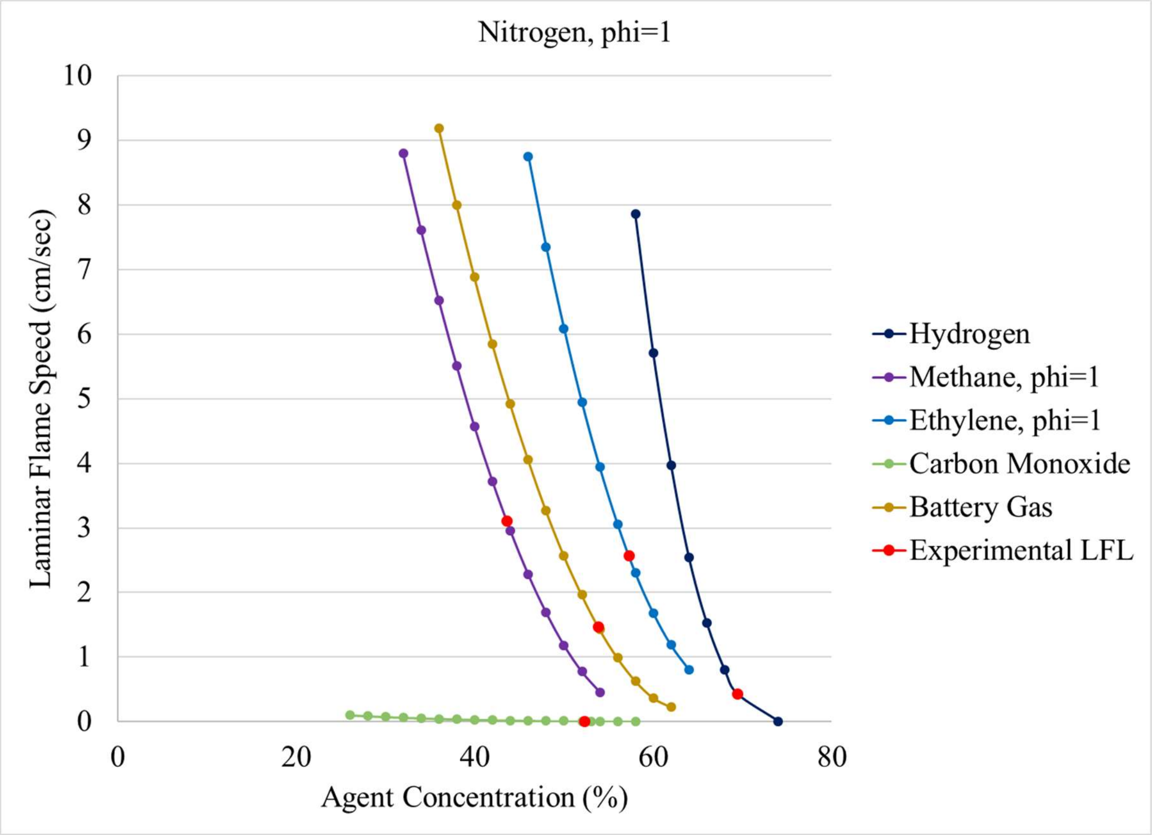


Figure 3.17: Variation of Laminar Flame Speed with Concentration of Nitrogen, phi=1

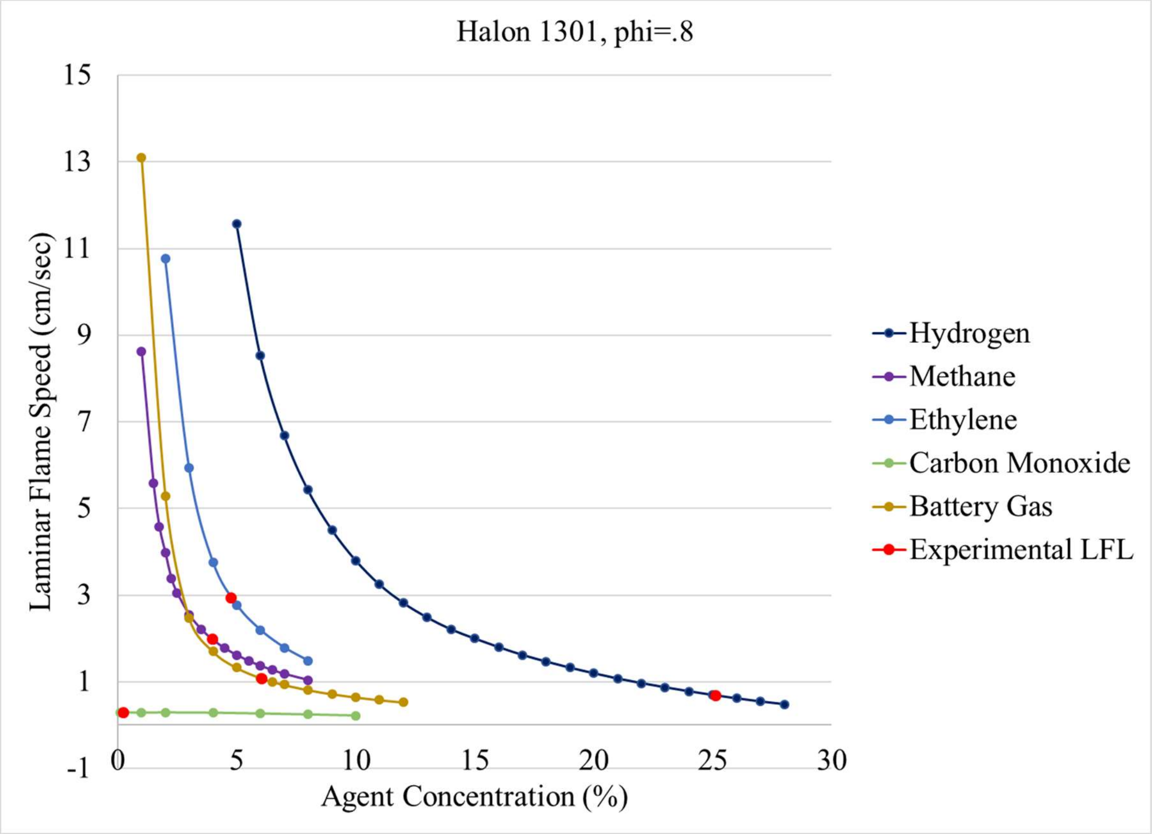


Figure 3.18: Variation of Laminar Flame Speed with Concentration of Halon 1301, phi=.8

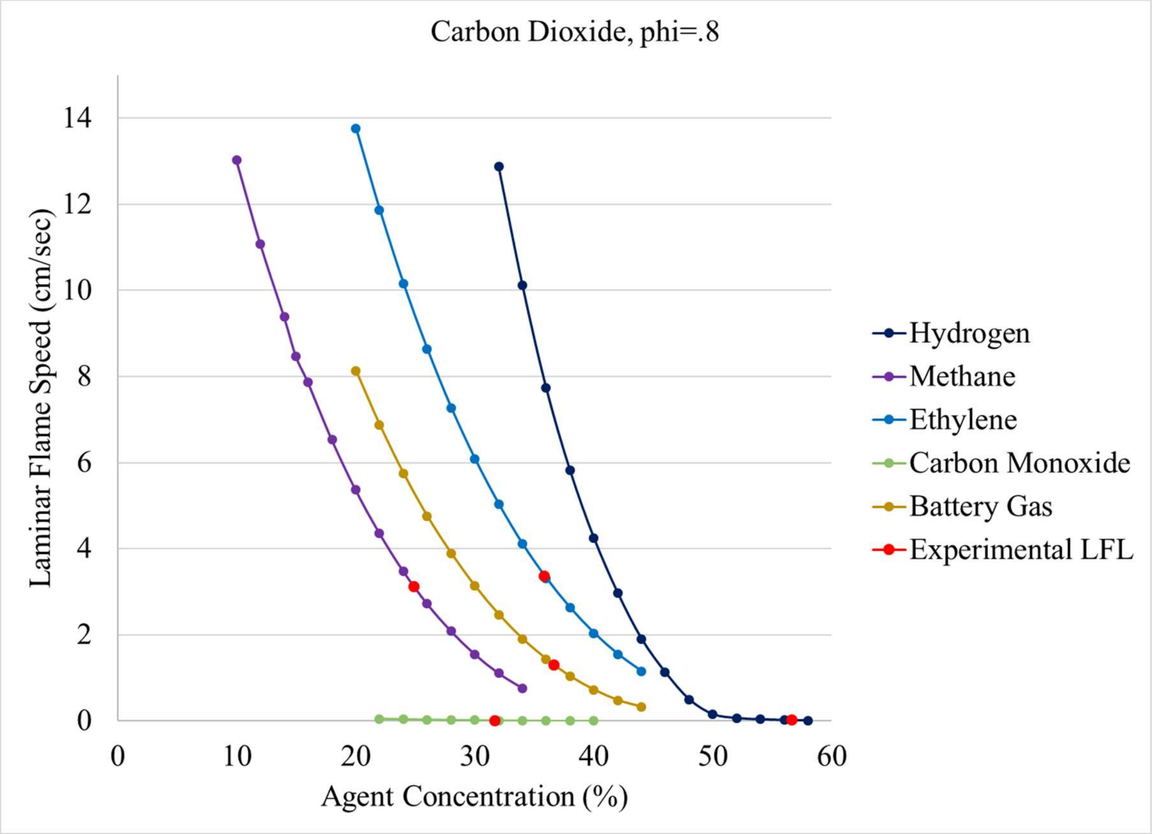


Figure 3.19: Variation of Laminar Flame Speed with Concentration of Carbon Dioxide, phi=.8

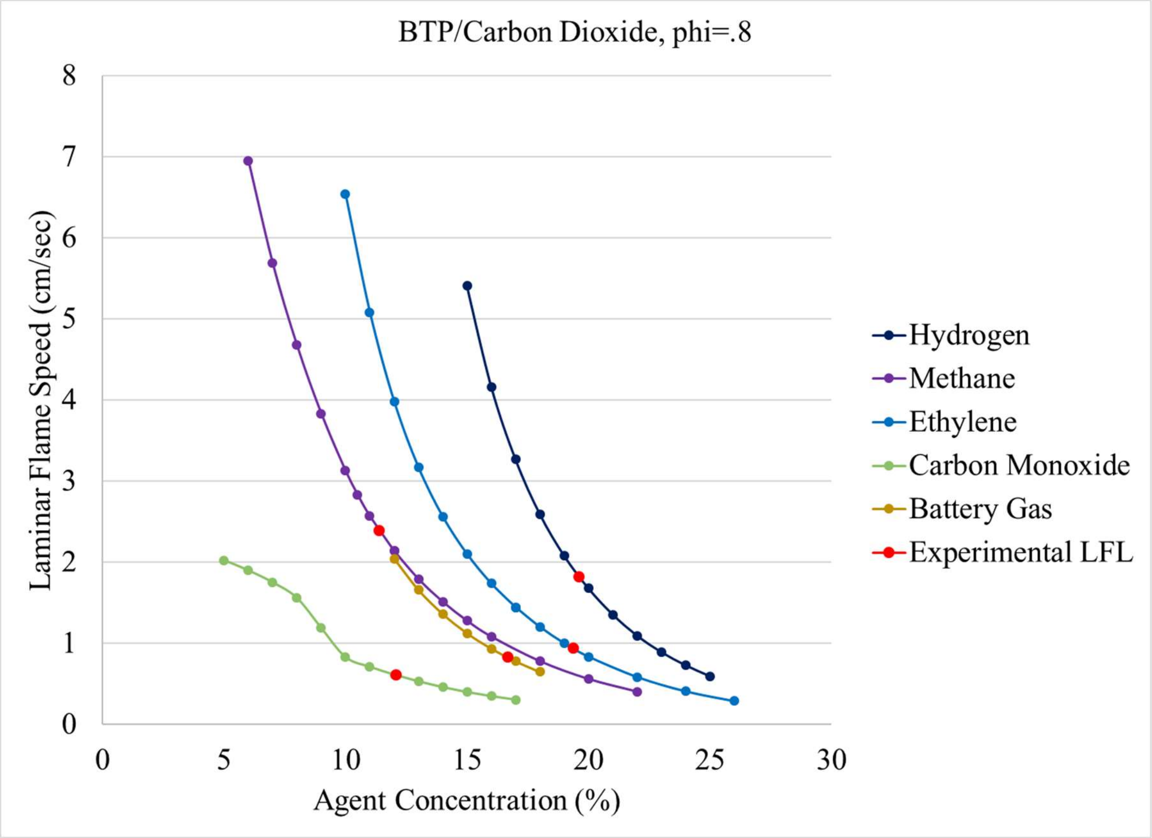


Figure 3.20: Variation of Laminar Flame Speed with Concentration of 2-BTP/Carbon Dioxide, phi=.8

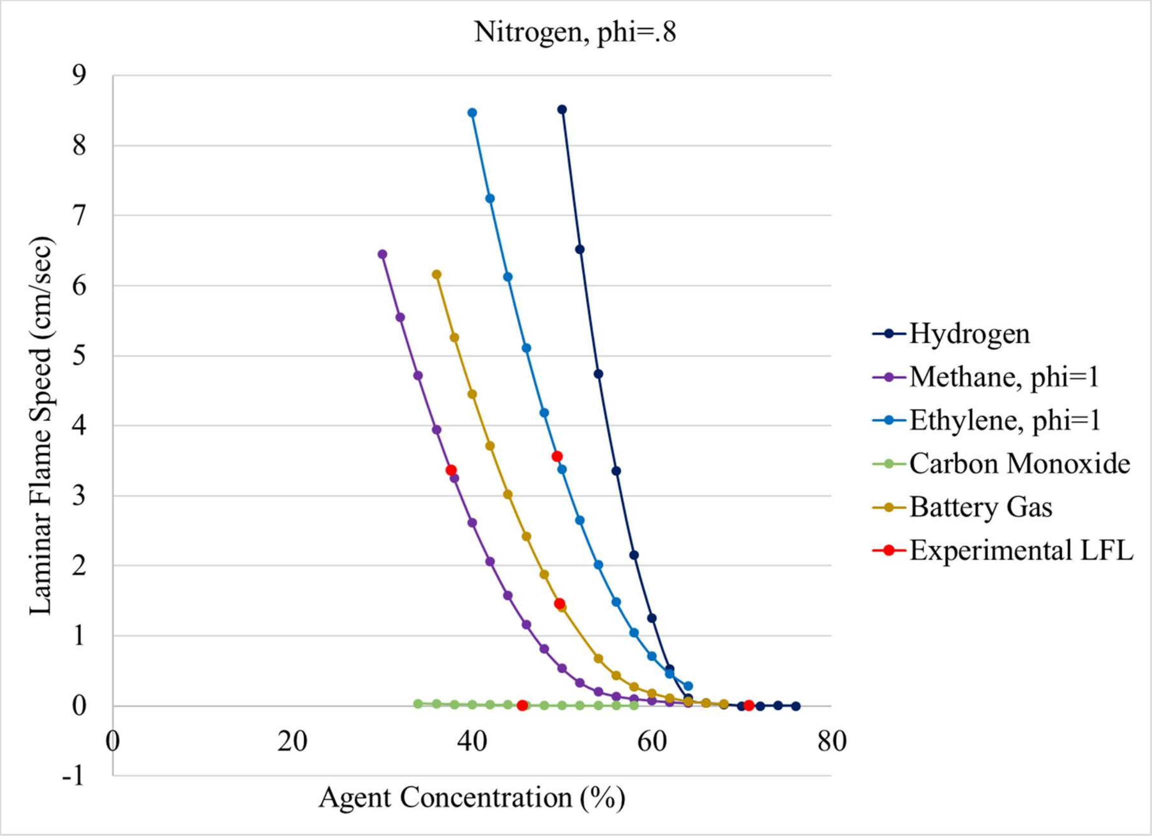


Figure 3.21: Variation of Laminar Flame Speed with Concentration of Nitrogen, phi=.8

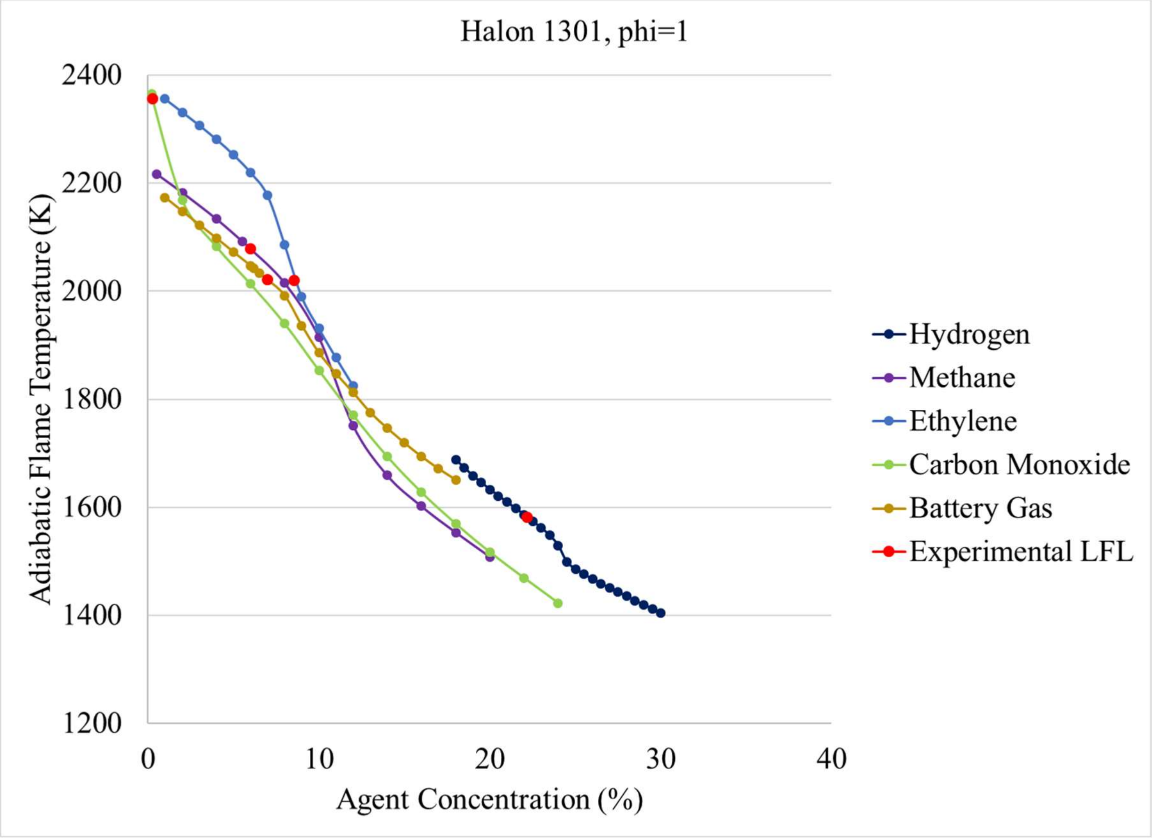


Figure 3.22: Variation in Adiabatic Flame Temperature with Concentration of Halon 1301, phi=1

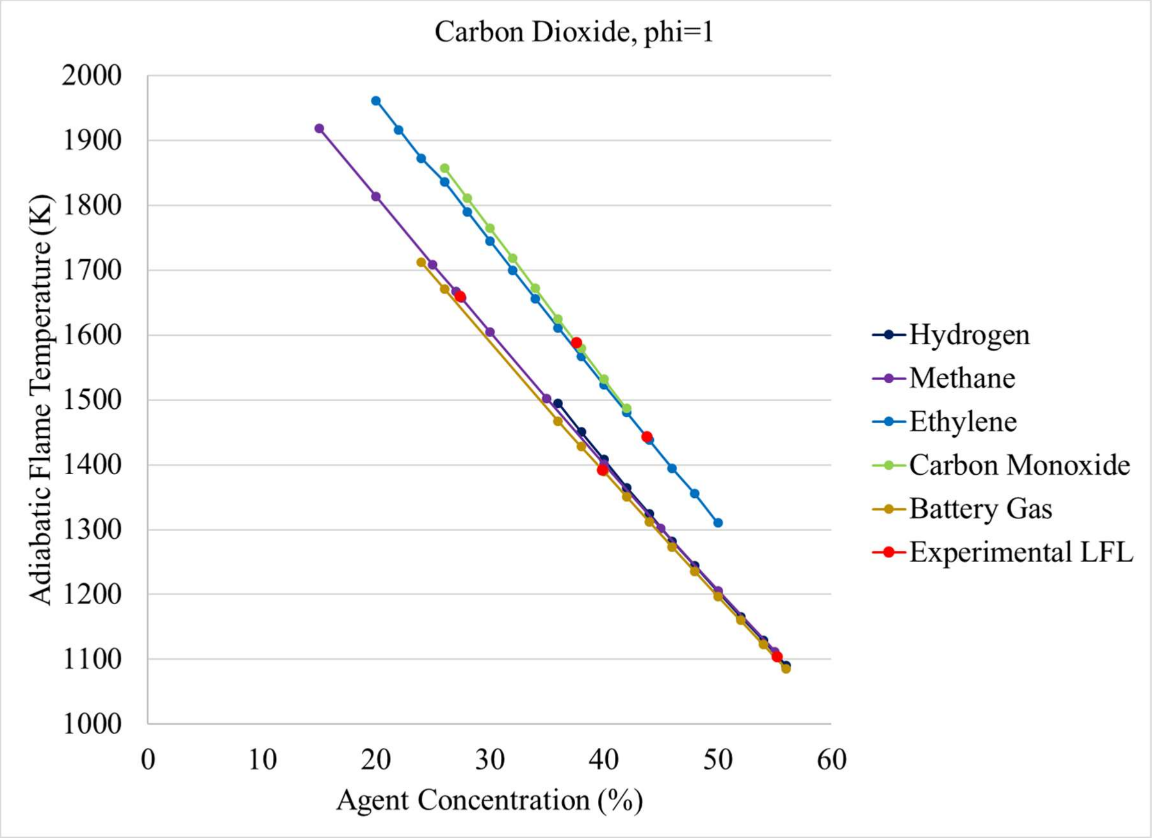


Figure 3.23: Variation in Adiabatic Flame Temperature with Concentration of Carbon Dioxide, phi=1

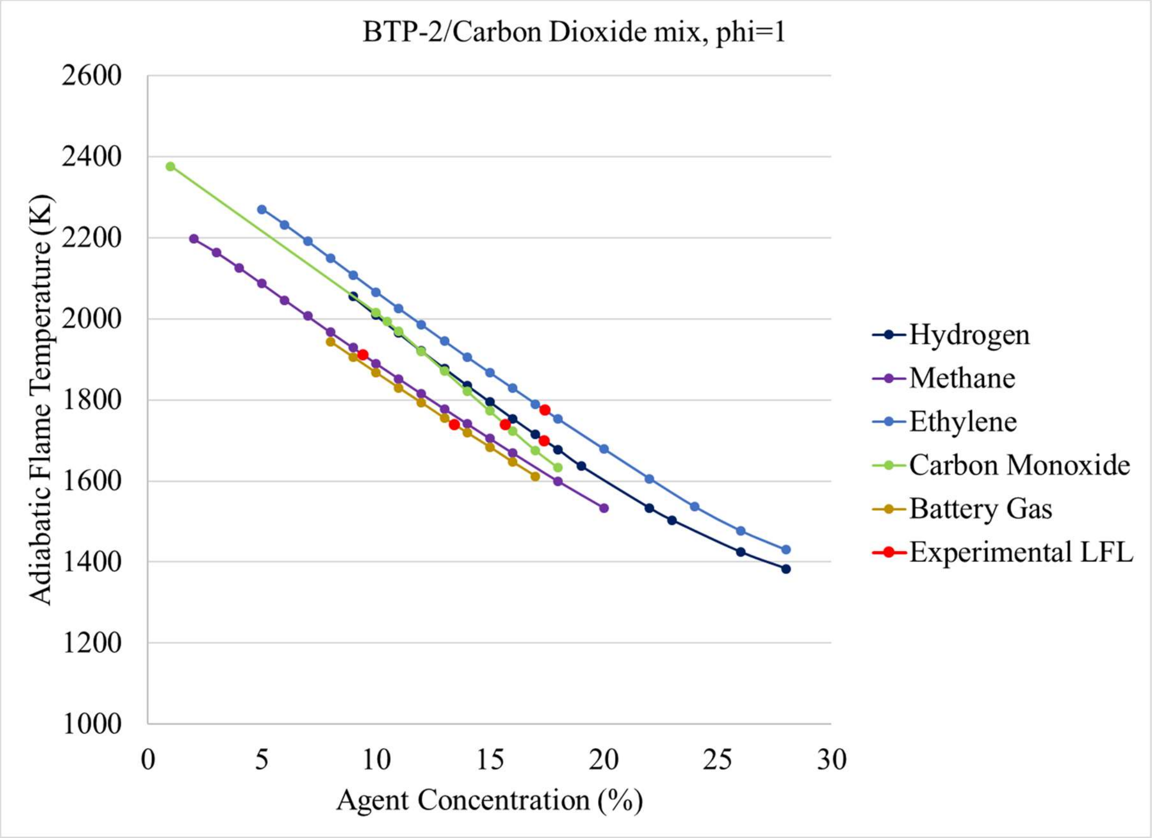


Figure 3.24: Variation in Adiabatic Flame Temperature with Concentration of 2-BTP/$CO_2$, phi=1

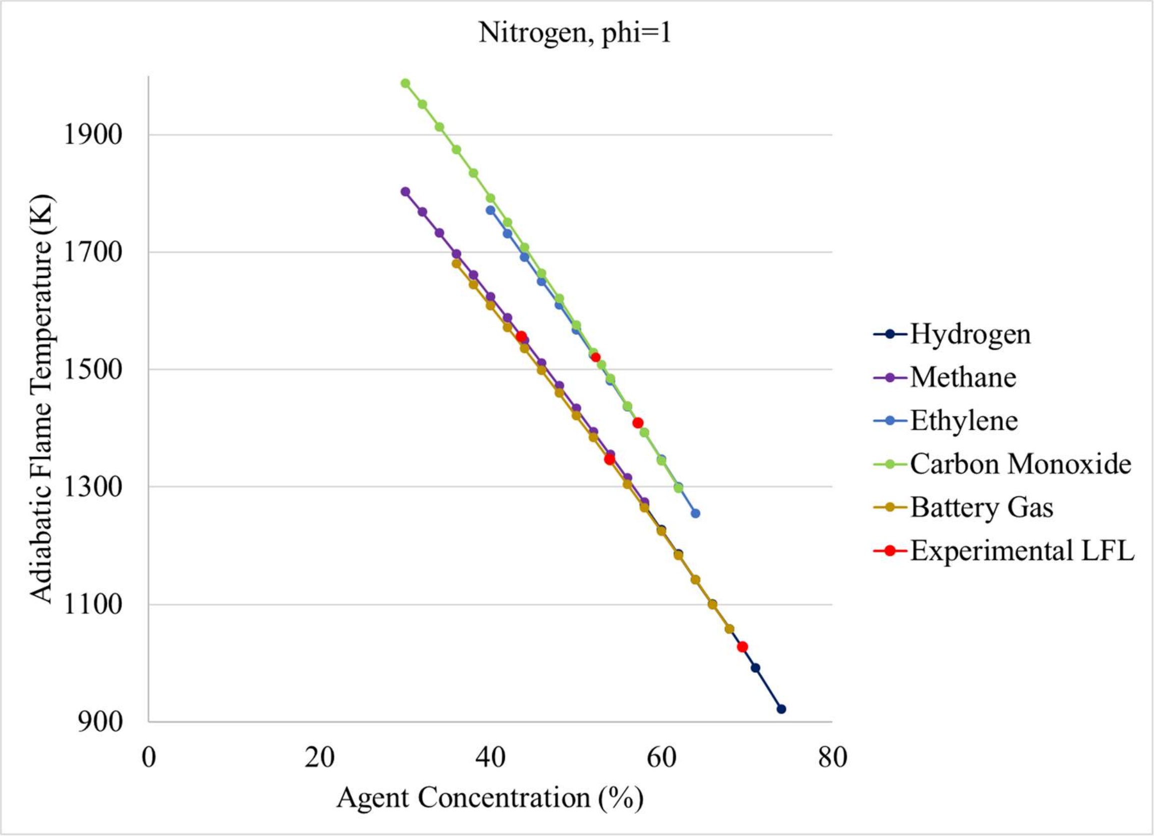


Figure 3.25: Variation in Adiabatic Flame Temperature with Concentration of Nitrogen, phi=1

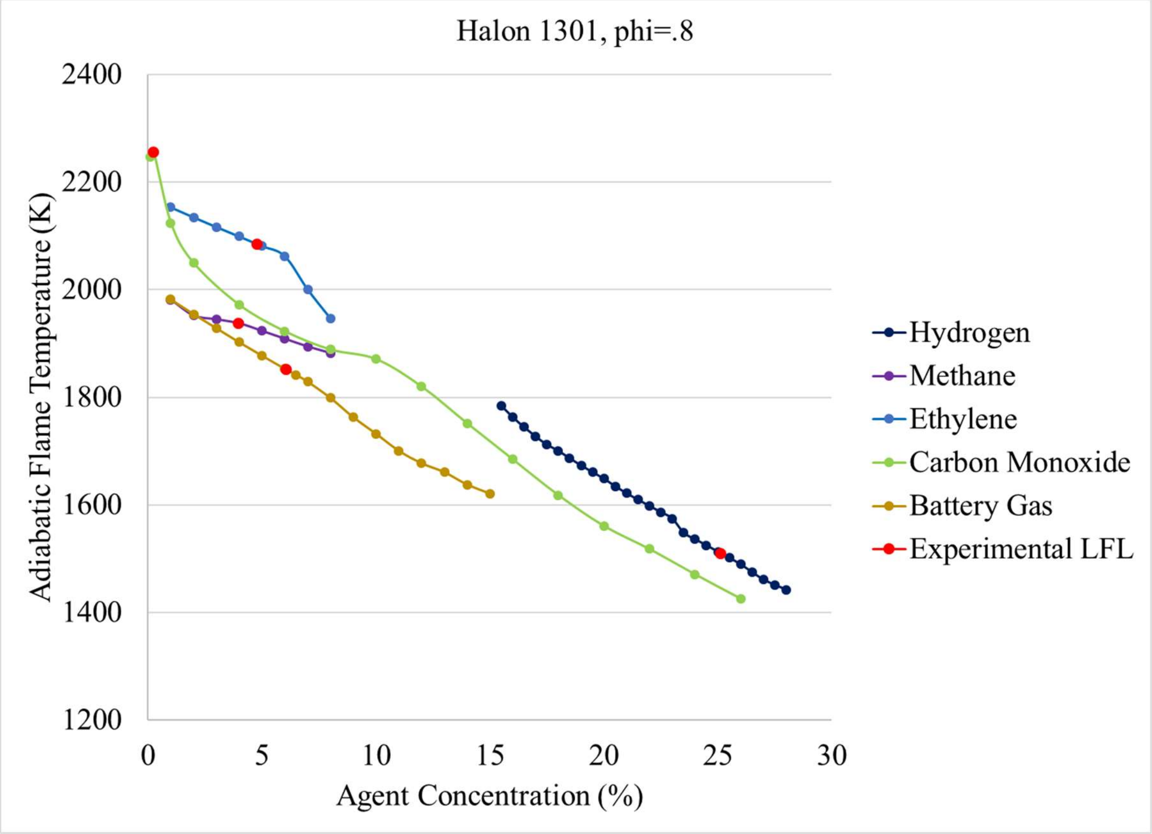


Figure 3.26: Variation in Adiabatic Flame Temperature with Concentration of Halon 1301, phi=.8

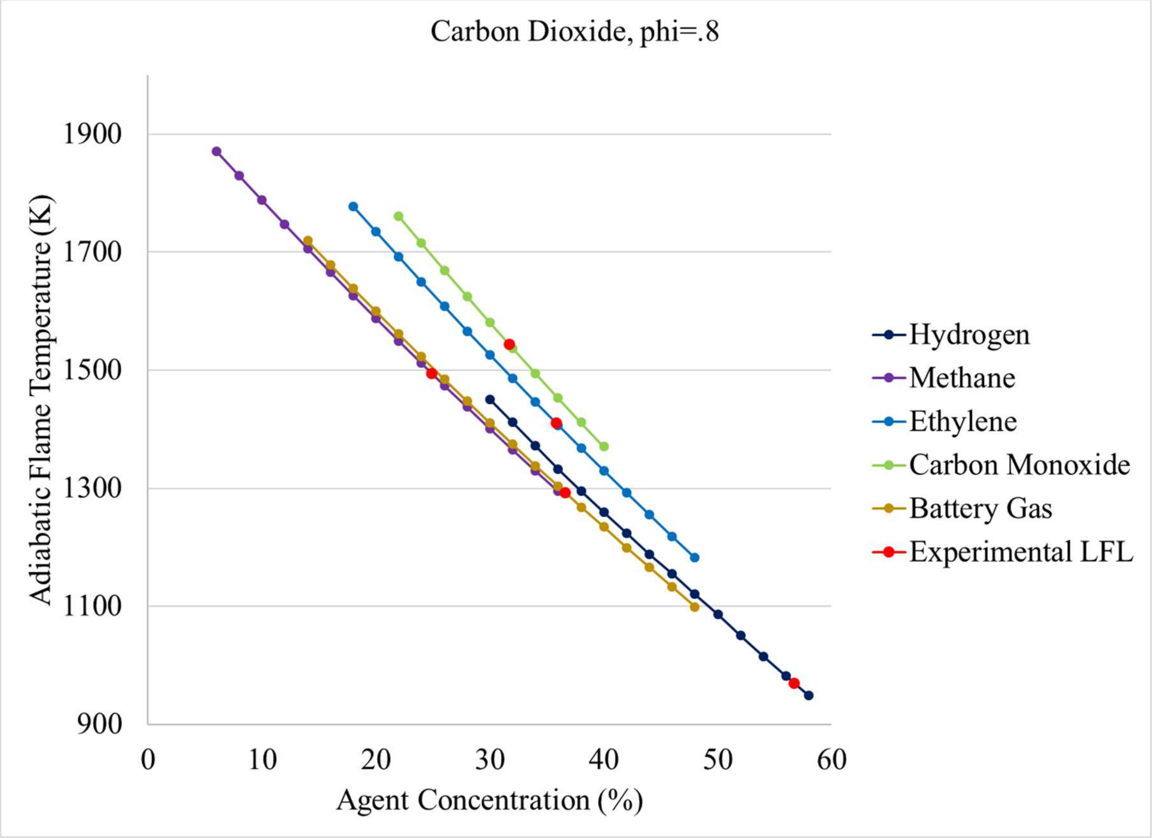


Figure 3.27: Variation in Adiabatic Flame Temperature with Concentration of Carbon Dioxide, phi=.8

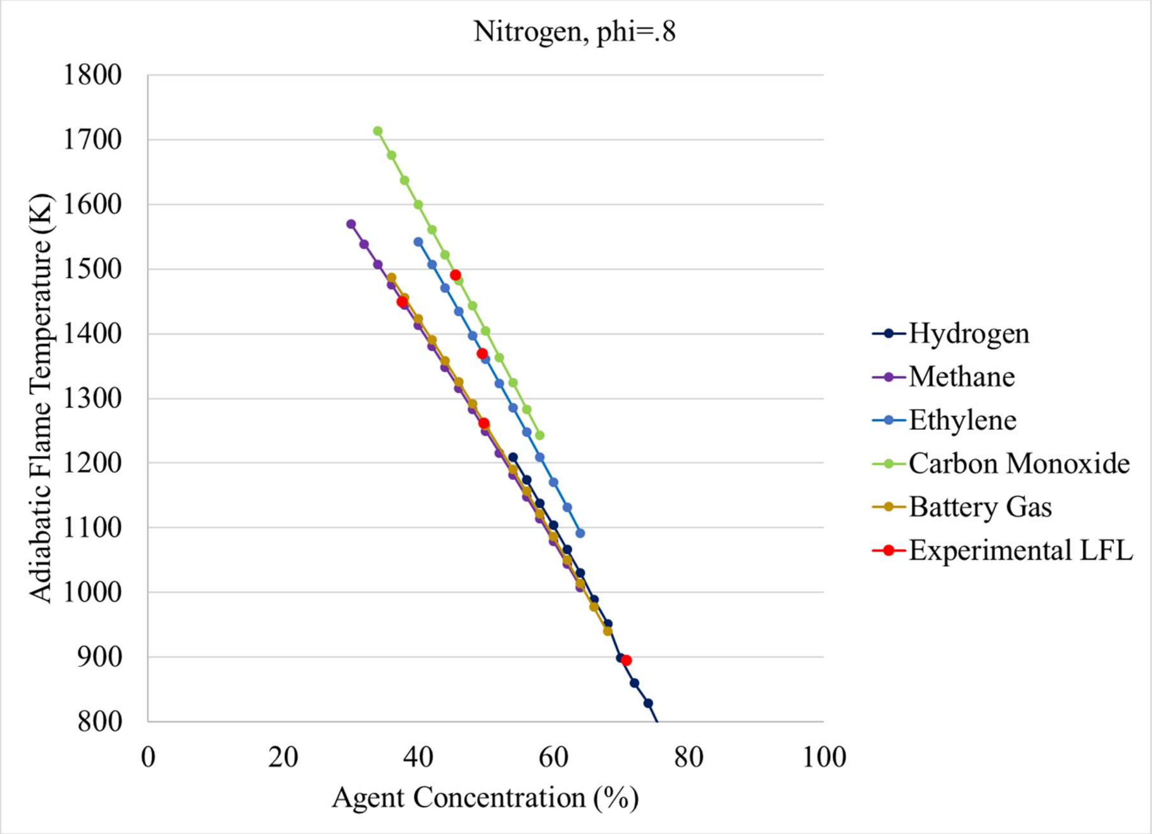


Figure 3.28: Variation in Adiabatic Flame Temperature with Concentration of Nitrogen, phi=.8

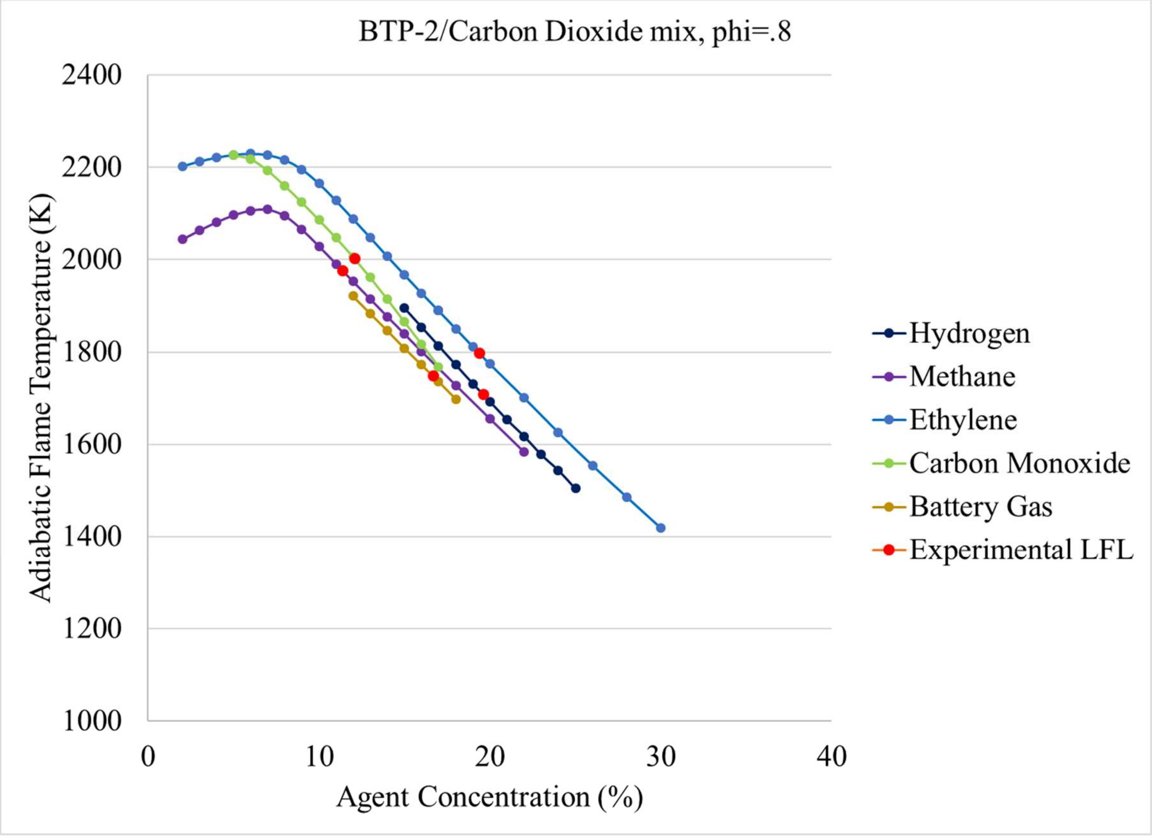


Figure 3.29: Variation in Adiabatic Flame Temperature with Concentration of 2-BTP/$CO_2$, phi=.8

Table 3.5: Flame Speeds Corresponding to Experimentally Found Inerting Concentrations of Extinguishing Agents (cm/sec)

| ***Simulation results, phi = 1*** | **Nitrogen** | **Carbon Dioxide** | **Halon 1301** | **2-BTP/$CO_2$ Mix** |
|---|---|---|---|---|
| *Hydrogen* | 0.43 cm/sec | .44 cm/sec | 1.15 cm/sec | 2.64 cm/sec |
| *Methane* | 3.10 cm/sec | 3.42 cm/sec | 2.26 cm/sec | 2.69 cm/sec |
| *Ethylene* | 2.57 cm/sec | 2.14 cm/sec | 1.79 cm/sec | 1.19 cm/sec |
| *Carbon Monoxide* | .008 cm/sec | 0.0113 cm/sec | .34 cm/sec | .27 cm/sec |
| *Battery Gases* | 1.46 cm/sec | 1.27 cm/sec | 1.55 cm/sec | 1.14 cm/sec |
| *Battery Gases 25k feet* | 2.20 cm/sec | 1.94 cm/sec | n/a | n/a |

Table 3.6: Adiabatic Flame Temperatures Corresponding to Experimentally Found Inerting Concentrations of Extinguishing Agents (deg. Kelvin)

| ***Simulation results, phi = 1*** | **Nitrogen** | **Carbon Dioxide** | **Halon 1301** | **2-BTP/$CO_2$ Mix** |
|---|---|---|---|---|
| *Hydrogen* | 1028.2 K | 1104.1 K | 1582.0 K | 1700.4 K |
| *Methane* | 1557.0 K | 1660.0 K | 2079.0 K | 1912.2 K |
| *Ethylene* | 1408.9 K | 1443.0 K | 2020.0 K | 1774.4 K |
| *Carbon Monoxide* | 1521.2 K | 1588.4 K | 2136.4 K | 1739.1 K |
| *Battery Gases* | 1347.5 K | 1392.2 K | 2021.5 K | 1738.7 K |
| *Battery Gases 25k feet altitude* | 1316.4 K | 1364.7 K | n/a | n/a |

Table 3.7: Laminar Flame Speed Corresponding to Experimentally Found Inerting Concentrations of Extinguishing Agents, phi = .8

| ***Simulation results, phi = .8*** | **Nitrogen** | **Carbon Dioxide** | **Halon 1301** | **2-BTP/$CO_2$ Mix** |
|---|---|---|---|---|
| *Hydrogen* | .0074 cm/sec | 0.019 cm/sec | 0.68 cm/sec | 1.82 cm/sec |
| *Methane* | 3.37 cm/sec | 3.12 cm/sec | 1.98 cm/sec | 2.39 cm/sec |
| *Ethylene* | 3.57 cm/sec | 3.37 cm/sec | 2.94 cm/sec | 0.94 cm/sec |
| *Carbon Monoxide* | 0.0108 cm/sec | 0.0143 cm/sec | 0.29 cm/sec | 0.61 cm/sec |
| *Battery Gases* | 1.46 cm/sec | 1.3 cm/sec | 0.9913 cm/sec | 0.83 cm/sec |

Table 3.8: Adiabatic Flame Temperatures Corresponding to Experimentally Found Inerting Concentrations of Extinguishing Agents, phi = .8

| ***Simulation results, phi = .8*** | **Nitrogen** | **Carbon Dioxide** | **Halon 1301** | **2-BTP/$CO_2$ Mix** |
|---|---|---|---|---|
| *Hydrogen* | 895.5 K | 969.8 K | 1510.2 K | 1707.9 K |
| *Methane* | 1450.2 K | 1494.3 K | 1938.1 K | 1975.9 K |
| *Ethylene* | 1369.9 K | 1410.2 K | 2085.2 K | 1798.3 K |
| *Carbon Monoxide* | 1491.0 K | 1544.3 K | 2030.7 K | 2002.4 K |
| *Battery Gases* | 1262.4 K | 1292.7 K | 1839.5 K | 1747.7 K |

Table 3.9: Predictions of Inerting Concentrations at 200°C Based on the Laminar Flame Speed that Corresponded to Experimentally Found Inerting Concentrations at 25°C, phi = 1

| ***Simulation results, phi = 1*** | **Nitrogen** | **Carbon Dioxide** | **Halon 1301** | **2-BTP/$CO_2$ Mix** |
|---|---|---|---|---|
| *Hydrogen* | 78.02 % | 64.32 % | 32.49 % | 23.38 % |
| *Methane* | 55.68 % | 37.4 % | 10.8 % | 15.6 % |
| *Ethylene* | 67.8 % | 54.4 % | 14.34 % | 23.93 % |
| *Carbon Monoxide* | 62.92 % | 47.82 % | n/a | 24.02 % |
| *Battery Gases* | 64.76 % | 49.95 % | 13.87 % | 20.16 % |

Table 3.10: Predictions of Inerting Concentrations at 200°C Based on the Adiabatic Flame Temperature that Corresponded to Experimentally Found Inerting Concentrations at 25°C, phi =1

| ***Simulation results, phi = 1*** | **Nitrogen** | **Carbon Dioxide** | **Halon 1301** | **2-BTP/$CO_2$ Mix** |
|---|---|---|---|---|
| *Hydrogen* | 76.05 % | 62.35 % | 24.56 % | 20.9 % |
| *Methane* | 50.896 % | 33.257 % | 8.98 % | 12.65 % |
| *Ethylene* | 63.6 % | 49.732 % | 10 % | 20.74 % |
| *Carbon Monoxide* | 58.68 % | 43.17 % | 3.85 % | 18.33 % |
| *Battery Gases* | 61.23 % | 46.53 % | 9.24 % | 17 % |

Table 3.11: Predictions of Inerting Concentrations at 25k feet Altitude Based on the Laminar Flame Speed that Corresponded to Experimentally Found Inerting Concentrations at Sea Level Pressure, phi = 1

| ***Simulation results, phi = 1*** | **Nitrogen** | **Carbon Dioxide** | **Halon 1301** | **2-BTP/$CO_2$ Mix** |
|---|---|---|---|---|
| *Hydrogen* | n/a | n/a | 22.5 % | 18.21 % |
| *Methane* | 49.47 % | 32.67 % | 6.69 % | 10.48 % |
| *Ethylene* | 60.34 % | 46.69 % | 8.92 % | 18.26 % |
| *Carbon Monoxide* | 52.36 % | 37.60 % | n/a | n/a |
| *Battery Gases* | 57.90 % | 44.03 % | n/a | 14.39 % |

Table 3.12: Predictions of Inerting Concentrations at 25k feet Altitude Based on the Adiabatic Flame Temperature that Corresponded to Experimentally Found Inerting Concentrations at Sea Level Pressure, phi =1

| ***Simulation results, phi = 1*** | **Nitrogen** | **Carbon Dioxide** | **Halon 1301** | **2-BTP/$CO_2$ Mix** |
|---|---|---|---|---|
| *Hydrogen* | 68.87 % | n/a | 21.09 % | 18.21 % |
| *Methane* | n/a | 26.90 % | 5.26 % | 9.28 % |
| *Ethylene* | 57.09 % | 43.28 % | 8.6 % | 17.24 % |
| *Carbon Monoxide* | 52.36 % | 37.53 % | n/a | n/a |
| *Battery Gases* | 53.77% | 39.62 % | n/a | 13.3 % |

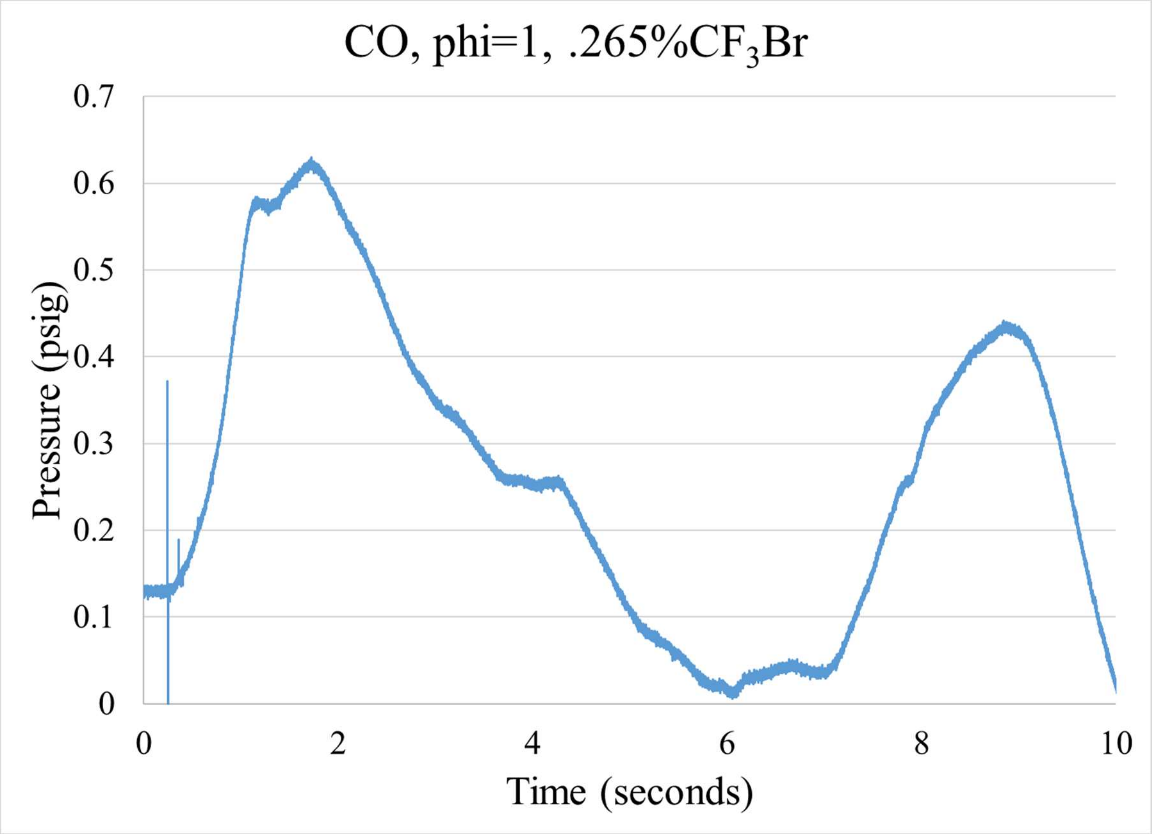


Figure 3.30 Pressure Rise Profile from Slow Propagation of Halon 1301/CO Flames

# 4. Error Analysis

In the latter part of this study, extinguishing agent concentrations were varied incrementally by 1% to 2% from one test to the next in order to find a concentration above and below the 5% (0.735psia) pressure rise criteria. Once these two concentrations were determined, linear interpolation was used to find a concentration that correlated to exactly 0.735psia. Because the concentration vs. pressure profiles were not linear, there was inherent error in the linear interpolation assumption.

Simulation tools like Cantera are based on kinetic, thermodynamic and transport parameters found in literature. Additionally, many assumptions are often made on the significance of individual elementary reactions within the overall reactions, leading to disregard of less-significant reactions and simplified mechanisms. Therefore, the overall model will only be as accurate and reliable as the parameters that are put into it. The primary focus of this study was experimental instead of numerical. Therefore, when simulations were conducted, the assumption was made that the input parameters to the model were completely accurate and all accuracy errors were related to the tolerance parameters that the model was run with. As mentioned previously, an analysis was performed to measure the accuracy of simulations based on simplifying model assumptions that were used such as “slope” and “curve” values as well as mixture average vs. multi-component diffusion. Assuming “slope” and “curve” values of 0.05 and a multi-component diffusion assumption was 100% accurate, the mixture-averaged assumption had an accuracy range of a fraction of a percent.

The mass measurement of 2-BTP was determined with a 1/4” calibrated tube. The tube was calibrated using a graduated syringe with ± 0.1 mL graduations. Polytetrafluoroethylene tubes are made with an inherent inner diameter tolerance and the quantity of measured 2-BTP varied accordingly. It was suspected that the error associated with this tolerance was negligible.

The Mettler XS204 scale that was used to measure aerosol mass had a labeled accuracy of .1mg. Therefore, the accuracy of the aerosol mass quantities within this study were within .002%.

The data acquisition module used for high-speed piezoelectric pressure measurements had an accuracy of 1.2 μV and the high-speed pressure sensor had an accuracy of ±1% FSO. The low speed pressure transducer had an accuracy of .05%.

# 5. Conclusions

This chapter summarizes the results found in this study and suggests applications for its significance to industry. Possible future work is proposed that will help gain further understanding into some of the findings that were discovered.

## 5.1. Summary of Results

First, experiments were performed to validate pressure-rise data measurements compared to literature and to map-out hydrogen and methane bell curves. Next, a few gases were tested at limiting concentrations of agent to quantify pressure-rise vs. agent concentration and quantify overpressure events. Finally, experiments and simulations were performed to quantify the amount of extinguishing agent needed for various flammable gases. Key findings were as follows:

- Halon 1301 experienced slight over-pressures with certain quantities of hydrogen. Rate-of-pressure-rise, however, was significantly reduced for all concentrations.
- Flame speed and adiabatic flame temperature found from simulations were shown to be a reasonable predictor of flammability.
- Halon 1301 was found to be extremely effective at suppressing carbon monoxide ignition when compared to other agents. It was hypothesized that this was related to the absence hydrogen in the reactants.
- Halon 1301 was significantly less effective against hydrogen than any other flammable gases tested.

- Nitrogen and carbon dioxide were 1.45% and 1.31% more effective against lithium battery gases at sea level pressure than at altitude. Simulations were conducted to predict required inerting concentrations for other agents and flammable gases and similar results were found. The difference was minimal between altitude and sea level pressure.
- 27.9% more carbon dioxide than nitrogen was required for battery gas inertion on a mass basis. However, on a volume basis, 35.1% more nitrogen was required than carbon dioxide.
- Hydrogen inerting generally occurred at a relatively low adiabatic flame temperature and carbon monoxide inerting occurred at a relatively high adiabatic flame temperature.
- The greatest amount of extinguishing agent was required for phi = 1 when compared to phi = 0.8 for all flammable gases and all agents except: hydrogen with carbon dioxide, hydrogen with Halon 1301 and 2-BTP/$CO_2$ with all flammable gases except carbon monoxide. For these combinations, a greater agent concentration was required at phi = 0.8.

## 5.2. Application to Industry

As mentioned, certification requirements currently utilize the "aerosol can" test as one of several tests to demonstrate a fire extinguishing agent's effectiveness. With more lithium batteries being shipped by air every year, it may be necessary in the future to develop additional extinguishing agent requirements to demonstrate that they are suitable for safe shipment of lithium batteries.

Unfortunately, there is nearly an unlimited number of possible combinations of flammable gases that can be expelled from a lithium battery and it is very difficult to predict how a new yet-to-be discovered extinguishing agent will behave with varied battery gas components. However, this study showed that minimum inerting concentrations can be predicted with reasonable accuracy by numerical simulation. If kinetic, thermodynamic, and transport mechanisms were developed for new extinguishing agents, flame speed, and flame temperature simulations would be possible. Results from this work could then easily be verified with experiment.

Nitrogen and carbon dioxide inert gases have been viewed as an attractive substitute for Halon 1301. The choice between $N_2$ and $CO_2$ will depend on a specific application. This study showed that $N_2$ was 21.8% more effective by mass against lithium battery gas and $CO_2$ was 26% more effective by volume. On an aircraft, both mass and volume are important to consider. For example: decreased mass has a direct correlation to decreased aircraft fuel burn. Whereas decreased volume has an indirect correlation to decreased fuel burn because it is much easier to maintain a decreased volume concentration in a leaking cargo compartment. Therefore, a smaller system may be possible.

In aircraft systems, care needs to be taken with extinguishment system design because of the dynamic environment with which fires occur. Even without combustion, lithium batteries produce enough heat to elevate a cargo compartment temperature. This would increase the quantity of extinguishing agent required. Additionally, ambient pressures are dynamic. Pressure alone was shown to have a slight effect on required extinguishing agent concentration but an even greater concern would be dilution of agent mixtures as an aircraft descends and oxygen flows into the compartment.

Currently, the required design concentration of Halon 1301 within an aircraft class-C cargo compartment is 5% “knockdown” followed by 3% “maintained”. Results from this study showed that 6.98% Halon 1301 was required to suppress battery gas at 25°C and approximately 14% was required at 200°C. Due to the increase of transportation of lithium batteries, higher concentrations of extinguishing agents may be necessary. Alternatively, other mitigation techniques to prevent or minimize lithium battery thermal runaway may also prove effective.

To utilize this approach to evaluate the effectiveness of new extinguishing agents or new mixtures of agents, the following approach is recommended:

1. Run simulations with various mixtures of the new agent and flammable gases. Consider inerting concentrations to occur at laminar flame speeds less than 4cm/sec.
2. Run experiments to validate the specific flame speeds at which inerting actually occurs for a few individual hydrocarbons, hydrogen, and carbon monoxide.
3. Re-run the simulations based on the inerting criteria found in step 2, to more closely define the concentrations at which inerting occurs. This will apply to additional mixtures of flammable gases and additional environmental conditions such as elevated temperature or reduced pressure.

## 5.3. Future Work

Further investigations could be conducted to explore the behavior of aerosol extinguishing agents. It was found that the method of adding the agent to an environment can affect its ability to suppress an explosion. More tests can be conducted to evaluate the difference between spark ignition and hot-surface ignition as well as the difference between ducting the aerosol into a vessel vs. directly activating it within a vessel.

Future work can be conducted to more precisely define the equivalence ratios associated with greatest required extinguishing agent concentrations. This will help give more insight into the behavior of individual reactions.

Additional work can be done to further characterize the effect of hydrogen addition to Halon 1301 and carbon monoxide mixtures as well as the role that water vapor has on combustion.

Additional work can be performed to optimize mixtures of extinguishing agents. For example, a 50/50 ratio of 2-BTP to $CO_2$ may not be optimal for all conditions. Other mixtures of gases can also be explored.

A test setup that allowed experiments to be conducted at elevated temperatures near 200°C would allow validation of predicted test results and provide a more accurate understanding of cargo compartment extinguishing agent concentrations that may be required.

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