DEVELOPMENT OF A SOLID-SOLID HYBRID GAS GENERATOR FIRE SUPPRESSION SYSTEM

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ABSTRACT

This paper addresses the advanced development of a novel solid-solid hybrid gas generator fire suppression technology to replace the ozone depleting Halon 1301 for total flooding applications. Mainstream's innovative solid-solid hybrid gas generator technology combines conventional gas generators with solid flame retardant materials. This combination will result in chemical extinguishment of the fire, as opposed to conventional gas generator technology which extinguishes the fire by physical (oxygen depletion) means. The technical objectives of this program were to evaluate and select improved inert gas generator (propellant) formulations, to package the propellant with the flame retardant inside the same housing, to evaluate various solid-solid hybrid system variables and select an optimum configuration that maximizes system performance, and to perform larger-scale fire suppression tests with the optimum configuration. Each of the objectives was successfully met.

Important findings include:

- Three gas generator formulations were selected for experimental evaluation: two non-azide gas generators and one azide gas generator. The non-azide propellants have high gas production efficiency but also generate unwanted water. The azide propellant generates only nitrogen gas but at low gas production efficiency.
- A housing configuration was developed and fabricated that contained both the propellant and the flame retardant.
- Experiments were performed to investigate the performance of the three propellants, the flame retardant type, and the ratio of propellant to flame retardant. The optimized configuration consisted of 20 grams of non-azide propellant with 50 grams of octabromodiphenyl oxide flame retardant in the divided bed configuration.
- Larger-scale fire suppression experiments were performed in a transient application, recirculating pool fire (TARPF) apparatus fabricated by Mainstream.
- The solid-solid hybrid gas generator generates various inert gases along with hydrogen bromide.

INTRODUCTION

The search for technologies that could be used in place of the ozone-depleting halons for fire suppression has been underway for over ten years. One alternative technology that is receiving interest is inert gas generation. Use of inert gas generators involves the activation of a thermochemical reaction in the gas generator that results in formation of the inert gases CO_2, N_2, and H_2O, as well as solid particulate byproduct. The product gases are emitted at temperatures ranging from 1200 °F to 2000 °F. Reports state that these systems are as effective as Halon 1301 on a mass basis. However, there are several drawbacks to conventional inert gas generator fire suppression systems:

1. Because inert gas generators suppress fires by physical means, significant quantities of inert gas are required to extinguish the fire. For example, the cup burner flame extinguishing concentrations (FEC) for nitrogen and carbon dioxide are 31.3 % (v/v) and 20.4 % (v/v), respectively, compared to Halon 1301 which has a flame extinguishing concentration of 3.0 % (v/v). A major improvement to this technology could be achieved if fire suppression by chemical extinguishment could be accomplished.
2. The inert gas exhaust is extremely hot, ranging from 1200 °F to 2000 °F.

Solid-liquid hybrid gas generation technology has also been explored to cool the hot exhaust gas. In these hybrid systems, the inert gas is discharged into a second pressure vessel containing a liquid fire suppression agent, which is pressurized and heated by the generated gas and discharged via a burst disk. These hybrid systems also have some drawbacks:

1. The hybrid systems require a second pressure vessel to store the liquid agent. This second storage vessel adds weight and size to the system.
2. The liquid fire suppression agents considered all have their own individual drawbacks. They are potential global warming gases and have long atmospheric lifetimes, and may face future environmental regulations.
3. The hybrid systems do cool the exhaust gas to below that of the gas generator only system, but the exhaust gas temperature is still hot and still a potential hazard.

Mainstream has developed an innovative solid-solid hybrid gas generator technology that addresses the drawbacks of the gas generator technologies described above (Ref. 1). Mainstream's hybrid system involves mixing the inert gas generator material with a solid, halogen-containing, flame retardant material. This halogen-containing flame retardant material has several functions:

1. Its decomposition results in the formation of radical scavenging decomposition products that serve as chemically-acting fire suppression agents and are subsequently delivered to the fire.
2. It serves as a heat sink for the exothermic gas generation reaction, resulting in delivery of a cool gas to the fire.

Examples of potential solid halogen-containing flame retardant materials include the wide variety of commercial bromine-containing flame retardants. These materials have melting points above room temperature where they would absorb significant energy due to their heat of fusion. They also decompose to form bromine radicals above 500°F. This decomposition would result in additional energy absorption as well as the formation of decomposition product radicals that would be delivered to the fire and be available to suppress the fire chemically.

Mainstream's innovative hybrid gas generator technology has many advantages over conventional inert gas generator systems and the hybrid systems that use liquid or vapor agents:

- Because chemically-acting agents in addition to the inert gases are delivered to the fire, the system is smaller and lighter than conventional inert gas generators.
- The chemically-acting agents delivered to the fire are bromine radicals, compared to fluorine radicals for other hybrid systems. Bromine radicals are known to be significantly more effective than fluorine radicals at fire suppression.
- Only one storage vessel is needed because the flame retardants are in the same vessel as the gas generator materials. This eliminates the need for a second storage cylinder, which is required for the solid-liquid hybrid systems.
- It has acceptable atmospheric properties and does not pose any global warming or ozone depletion threat during manufacturing, storage, and handling. Upon release, the bromine-containing materials are in a very reactive form and will be removed readily by the fire or in the troposphere.
- The flame retardant materials are of low toxicity or are nontoxic.
- The flame retardant materials are available in many forms and sizes.
- These flame retardant materials are readily available and inexpensive.

EVALUATION OF GAS GENERATOR FORMULATIONS

Both azide and non-azide gas generator formulations were evaluated. Azide formulations have the advantage of generating essentially 100 % nitrogen gas (no water), however, their gas production efficiencies are typically only 50 % or less. Non-azide formulations have the advantage of gas production efficiencies that are much higher than the azide formulations, but have the disadvantage of generating water along with other inert gases. Water is undesirable, because it combines with the bromide ions generated by the flame retardant decomposition to form HBr. Table 1 provides information on the effluent of the gas generators.

DEVELOP PROTOTYPE HOUSING FOR SOLID-SOLID HYBRID GAS GENERATOR

Figure 1 depicts the prototype housing configuration. The design incorporates a standard one-inch outer diameter, 3/32 inch wall, low carbon steel tubing. The tubing can be cut to length for a given propellant and flame retardant load. A standard automotive initiator interface is laser welded to the tube. An elastic initiator seal is compressed between the initiator and the initiator interface through a crimp. This seal provides a hermetic seal for this interface. A spring-loaded generant cup, with a slip-fit in the tube, pre-loads the propellant bed to minimize rattle noises and propellant vibration damage. The pre-load minimizes free spaces among the pellet bed. The generant cup, with its small hole array, contains the propellant pellets during its combustion. Without this generant cup, the burning pellets would be ejected from the housing through the large-sized nozzle. A retainer, press-fit into the tube, is the separator screen between the generant and the flame retardant. The retainer has a foil seal to prevent material transfer between the generant and the flame retardant. The ballistic nozzle is the last component of the housing assembly. A copper foil seal is adhered over the nozzle. It is press-fit into the tube and then laser welded. A silver nitrate based autoignition material is built into the unit as a safety feature. This material autoignites above 134 °C.

Table 1 – Comparison of Gas Generator Effluent

Formulation	Azide	Non-Azide #1	Non-Azide #2
% Gas Production	43.3 %	87.3 %	68.55 %
wt % N_2	0.29	32.2 %	4.83 %
wt % H_2O	0.00	32.0 %	15.54 %
wt % CO_2	0.00	21.4 %	48.18 %
wt % Other Gases	0.02	1.7 %	< 0.1 %
Moles of Gas (per 20 g propellant)	0.31	0.69	0.42
% Solids Production	56.8 %	12.7 %	31.45 %
moles copper	0.09	0.00	0.07
moles sodium chloride	0.00	0.03	0.03
moles sodium oxide	0.09	0.00	0.00

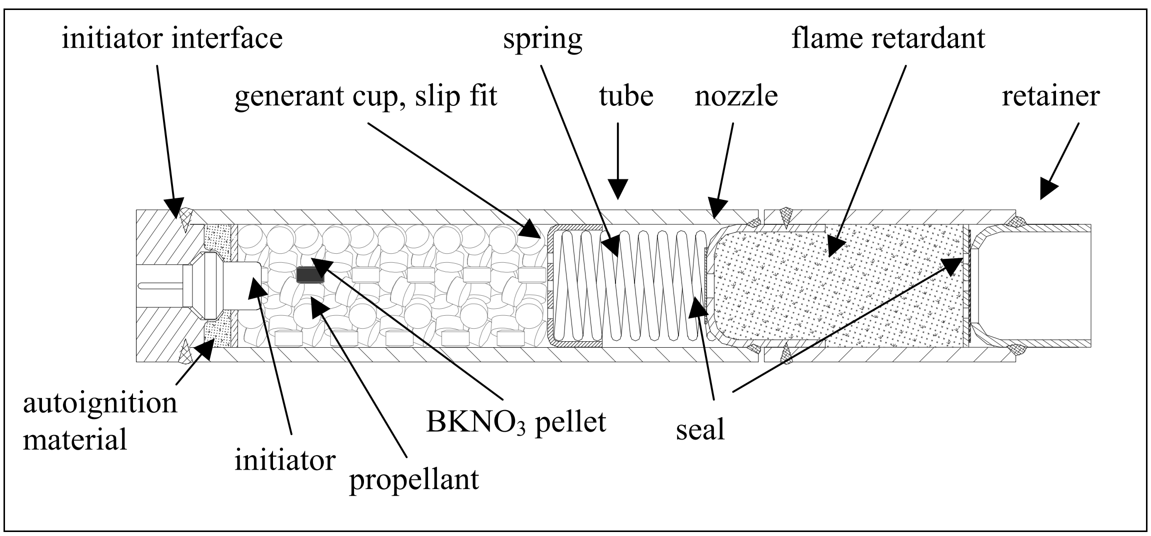

Figure 1. Final design of gas generator housing configuration.

OPTIMIZE PERFORMANCE OF SOLID-SOLID HYBRID GAS GENERATOR SYSTEM

To optimize the performance of the solid-solid hybrid gas generator the following experimental variables were examined: propellant type (azide and non-azide), flame retardant type (decabromodiphenyl oxide and octabromodiphenyl oxide), and the ratio of propellant to flame retardant. The experimental results that were used to determine the optimum conditions are minimizing cup burner FEC and maximizing the amount of bromine and bromide ion formation.

The experimental apparatus consisted of a gas generator housing designed to accommodate the geometry of the gas generator housing, a gas collection vessel, and a sample cylinder. The function of the gas collection vessel is to collect the expelled gases from the gas generator housing for FEC measurements in the cup burner apparatus. It consists of a 3.785-liter stainless steel sample cylinder that has been modified with a flange at one end for connection to the gas generator housing (modified volume of 4175 ml). The end of the gas collection vessel opposite the flange has a needle valve and a connection to the gas sample cylinder. The function of the gas sample cylinder is to collect a representative sample of generated gases for subsequent analysis for bromine and bromide ion. It is a 50 ml stainless steel sample cylinder with a Teflon lining and needle valves at both ends.

The inert gas generator was ignited using a 12 VDC power supply. Prior to ignition, the experimental apparatus was evacuated to remove any air from the system. System temperatures and pressures were noted before and after ignition. The pressure transducer and thermocouple used in the apparatus did not have a fast enough response to measure the peak temperature and pressure, only the final static pressure and temperature were noted.

Once detonation of the inert gas generator and flame retardant was complete and the gas collection vessel had reached a stable temperature and pressure, the sample cylinder was separated from the gas collection vessel and weighed. The sample cylinder was then attached to a gas sparging trap containing deionized water. Once attached to the gas trap, the valve connecting the sample tank to the gas trap was opened to allow the positive pressure to push gas into the gas trap. When the pressure equalized to atmospheric pressure, the valve on the opposite end was opened to allow pressurized air to enter the sample tank and purge all the remaining gas into the gas trap. Any bromine or bromide present in the gas was stripped by the water present in the gas trap and prepared for further analysis.

Bromine analysis was performed on the deionized water used in both the gas trap and extraction. The reason for using deionized water over an alkaline aqueous solution was to preserve molecular bromine (Br_2). The method for bromine analysis relied on a bromine reagent that reacts to oxidizing substances such as bromine. As this oxidation process occurs, the color changes from clear to red in direct proportion to the bromine concentration. A measurement was taken by passing a light beam through the sample and measuring the absorbance. Mainstream utilized a factory calibrated, hand held spectrophotometer to accomplish this task. This meter was calibrated for a range of 0.0 to 8.0 mg/L Br_2 and the bromine concentrations read directly from a LCD display.

Bromide analysis utilized a 0.125 M NaOH solution to insure that all the bromine was in the form of bromide and that all samples had a consistent ionic strength. Part of the deionized water containing the trapped or extracted bromine was made basic by adding sodium hydroxide until the concentration reached 0.125 M NaOH. The bromide ion was measured potentiometrically using a bromide ion-selective electrode in conjunction with a single junction, sleeve-type reference electrode. Calibration was accomplished by reading electrode potentials in millivolts when exposed to 0.125 M NaOH solutions containing known amounts of bromide (0-1000 mg/L Br^-).

Experiments were performed to examine the effect of propellant type (azide or non-azide), flame retardant type (decabromodiphenyl oxide or octabromodiphenyl oxide), and a low or high ratio of flame retardant to propellant. The experimental results used to determine the optimum conditions will be those that minimized the cup burner flame extinguishing concentration, maximize the bromine/bromide ion formation and percent yield of bromine and bromide ion.

The experimental results with the azide formulation and non-azide formulation #2 were disappointing, resulting in no extinguishment in the cup burner apparatus or high values of a cup burner FEC. The moles of bromine and bromide ions formed with those two gas generator formulations are much lower than theoretical. A plausible explanation for the poor experimental results with those two formulations may be explained by examination of the effluent of the formulations, which is provided in Table 1. The non-azide #2 formulation generates 0.42 moles of gas, the azide formulation generates 0.31 moles of gas. This compares to the non-azide #1 formulation, which generates 0.69 moles of gas. Thus, further work with the azide formulation and non-azide #2 formulation was halted.

Experiments continued with non-azide formulation #1. There were only two variables to examine: the flame retardant type (decabromodiphenyl oxide and octabromodiphenyl oxide) and the ratio of flame retardant to propellant. Ten experiments were performed, plus duplicates of each, giving a total of twenty experiments. The matrix involved using 20 grams of non-azide formulation #1 in the divided bed configuration. Table 2 presents a summary of the cup burner results from the experiments. For each flame retardant type and amount, Table 2 lists the cup burner FEC of the two experiments and the average FEC.

Bromine and bromide ion analysis of both the gas phase and residue phase were also performed using methods described previously. These results are presented in Table 3. The analysis results presented in Table 3 represent the average values from the duplicate experiments. Table 3 shows that there is significantly more bromide ion formed than molecular bromine.

Table 2 – Summary of Cup Burner Results for Non-Azide Formulation #1

Flame Retardant Type	Flame Retardant Amount	FEC 1	FEC 2	Average FEC
Octabromodiphenyl oxide	10 grams	n/a[1]	45 %	45 %
	20 grams	n/a[2]	34 %	34 %
	30 grams	23 %	26 %	25 %
	40 grams	18 %	17 %	17 %
	50 grams	13 %	14 %	14 %
Decabromodiphenyl oxide	10 grams	58 %	54 %	56 %
	20 grams	34 %	n/a[1]	34 %
	30 grams	No Ext.	29 %	29 %
	40 grams	30 %	23 %	27 %
	50 grams	15 %	19 %	17 %
Notes: [1] gas sample leaked out of gas collection vessel [2] insufficient amount of gas to extinguish flame				

Table 3 – Summary of Bromine and Bromide Ion Analysis Results

Flame Retardant Type	Flame Retardant Amount	Gas Phase		Residue Phase	
		Moles Bromide	Moles Bromine	Moles Bromide	Moles Bromine
Octabromodiphenyl oxide	10 grams	5.45E-02	3.61E-06	1.50E-01	0.00E+00
	20 grams	4.92E-02	2.99E-07	3.02E-01	0.00E+00
	30 grams	1.33E-01	0.00E+00	7.11E-02	0.00E+00
	40 grams	2.28E-01	0.00E+00	5.50E-02	0.00E+00
	50 grams	3.34E-01	9.33E-05	8.87E-02	0.00E+00
Decabromodiphenyl oxide	10 grams	6.96E-02	6.55E-06	5.36E-02	0.00E+00
	20 grams	4.85E-02	5.23E-06	8.77E-02	0.00E+00
	30 grams	1.55E-01	5.64E-06	5.99E-02	0.00E+00
	40 grams	1.44E-01	1.59E-05	3.05E-02	0.00E+00
	50 grams	3.73E-01	4.65E-06	6.68E-02	0.00E+00

Figure 2 is a plot of the average flame extinguishing concentration versus the flame retardant mass. These figures show an expected decrease in FEC with increasing flame retardant mass and bromide ion formed. The FEC appears to be reaching a minima at 50 grams of flame retardant. The data also shows that octabromodiphenyl oxide appears to perform slightly better than decabromodiphenyl oxide. Figures 3 is a plot of the moles of bromide versus the amount of flame retardant. As expected, the amount of bromide increased as the amount of flame retardant increased.

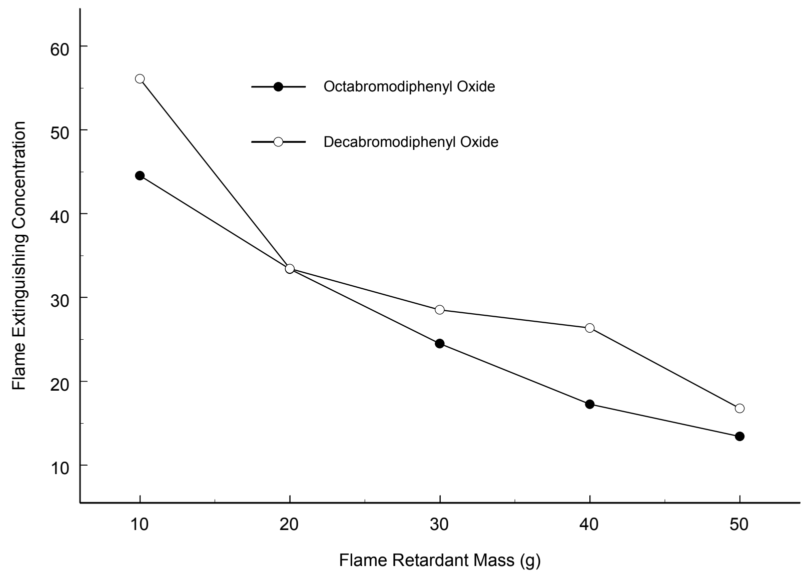

Figure 2. Average FEC versus amount of flame retardant.

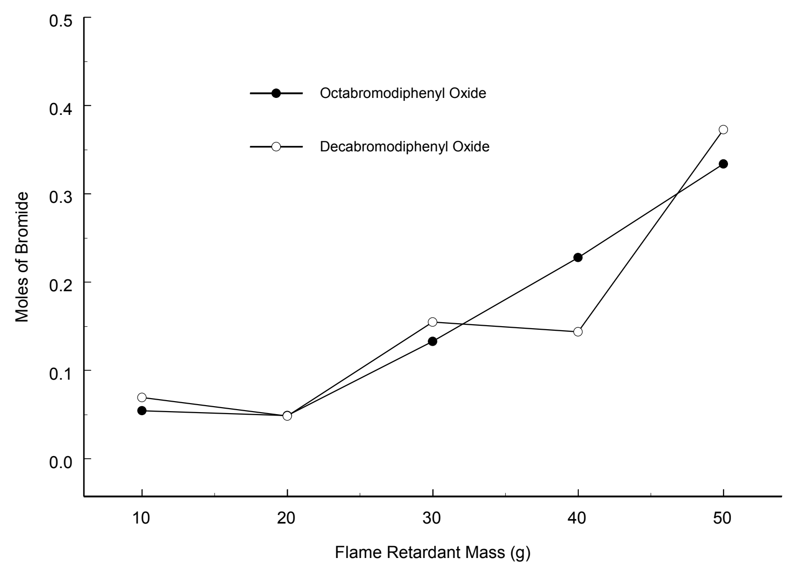

Figure 3. Moles of gas-phase bromide formed versus amount of flame retardant.

PERFORM LARGER-SCALE FIRE SUPPRESSION EXPERIMENTS

The goal of the larger-scale experiments was to take the optimized solid-solid hybrid gas generator configuration and perform larger-scale fire suppression experiments, beyond cup burner evaluations. Another goal was to compare the solid-solid hybrid configuration to a conventional inert gas generator (no flame retardant). It was decided to use the NIST Transient Application Recirculating Pool Fire (TARPF) agent screen apparatus for these tests. The TARPF has a back-facing step in a wind tunnel with a recirculation zone over a pool of fuel by the step (Ref. 3). Since the NIST TARPF apparatus could not be made available to Mainstream for testing, we reviewed the drawings and information contained in Reference 3 and designed and fabricated a TARPF apparatus at Mainstream. The goal was to design an apparatus with features and dimensions as close to the NIST apparatus as possible.

Mainstream's TARPF is a small wind tunnel consisting of a pool burner assembly, an entrance section, an exhaust section, a diffuser assembly, and an agent injector assembly. The overall dimensions are 1.8 meters long with a square cross section of 102 mm on a side. The tunnel is constructed of 1018 mild steel. Air is supplied by a variable speed blower controlled by a DC power supply. Air flow is monitored using a hand-held digital anemometer. A honeycomb flow straightener is located upstream of the diffuser section. The burner consists of a sintered bronze plate, 95 mm wide by 190 mm long. There is a 13 mm backward facing step upstream of the burner. Propane is the fuel supplied to the burner, controlled by a rotameter. The fire is initiated by a spark across two electrodes on the side wall. The fire is viewed from above and the side through Pyrex windows. Figure 4 is a photograph of the entire apparatus and Figure 5 is a photograph of the burner section.

For injection of the gas generators, a discharge chamber similar to the one NIST uses to inject gas generators in their TARPF was designed and fabricated. In this approach, the operator selects the fraction of the gas generator that is injected into the flame zone by placing appropriate orifice plates on an injection manifold and on a bypass line. The area of the orifice on the supply line and of the orifice on the bypass line determine the fraction of agent injected. The bypass line leads directly to a fume hood. Orifice plates with diameters ranging from 1/32 of an inch to 1/2 inch were fabricated. The manifold accommodates the gas generator housing. This approach was necessary because both the conventional gas generators and the solid-solid hybrid gas generators contain significantly more material than is needed for suppression in the TARPF.

Results Using Conventional Gas Generators

A total of 10 conventional gas generators were procured for testing on this effort. They all contained 20 grams of non-azide formulation #1 propellant, which will generate 17.5 grams of inert gas (see Table 1 for composition of gas). For the experiments, the air flow was set to 5.4 m/s and the propane flow was set at 85 ml/s. These are the same flow conditions that NIST used in the TARPF apparatus when testing gas generators.

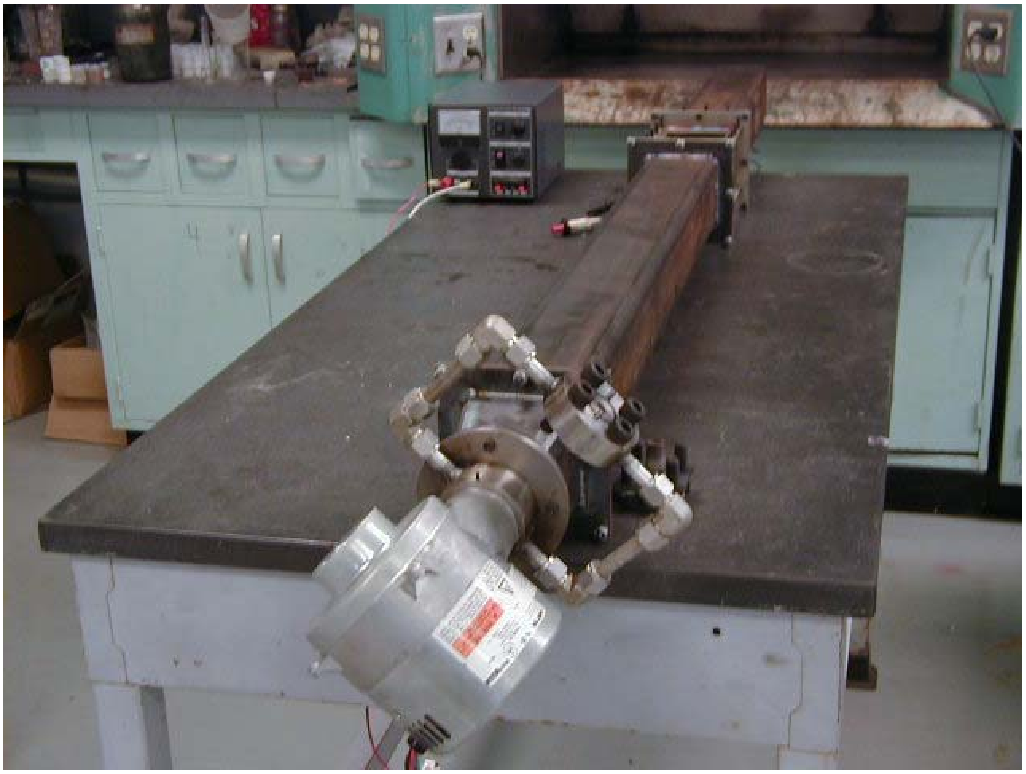

Figure 4. Photograph of Mainstream's TARPF apparatus.

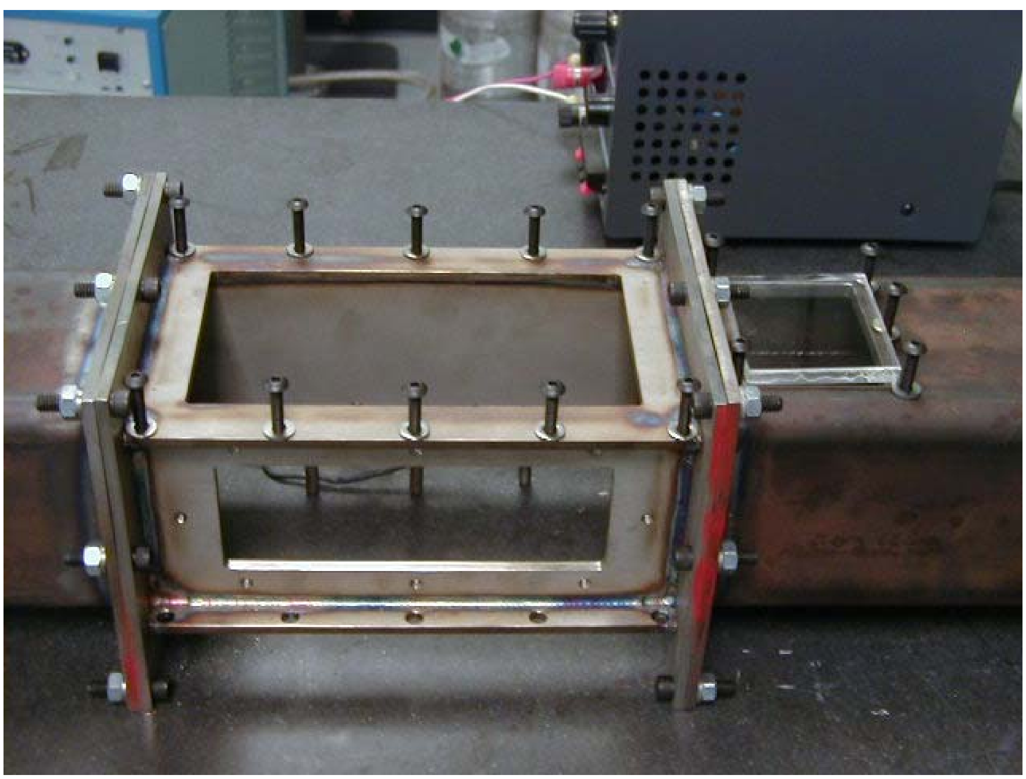

Figure 5. Photograph of burner section.

Table 4 presents the test results for the conventional gas generators. The goal is to determine for a given mass of gas supplied to TARPF, whether or not the fire could be suppressed. The mass of gas supplied to TARPF is the total amount of gas generated (17.5 grams for the conventional gas generators) multiplied by the % open area to TARPF (the remaining gas goes to the bypass stream). Table 4 shows that 0.38 grams of inert gas suppressed the fire 0 % of the time, 0.67 grams of inert gas suppressed the fire 33 % of the time, 1.03 grams of inert gas suppressed the fire in its only test, and 1.75 grams of inert gas suppressed the fire out in its only test.

More tests at the 1.03 and 1.75 gram level need to be performed to more fully determine what percentage of the fires could be suppressed versus the amount of gas supplied. Unfortunately, timing and funding limitations prevented procurement and testing of additional gas generators. However, it appears that one could expect 100 % suppression if 1.03 – 1.75 grams of inert gas is supplied to TARPF and 33 % suppression when 0.67 grams is supplied. This conclusion generally agrees with the NIST results for gas generators in TARPF (Ref. 3), which found that suppression was successful if at least 1.5 grams of agent was supplied to the fire, and extinction never occurred when less than 0.7 grams was supplied.

Table 4 – TARPF Test Results for Conventional Gas Generators

% Open Area to TARPF	Mass of Gas to TARPF	Result
0.00 %	0.00 grams	Fire Not Suppressed
2.20 %	0.38 grams	Fire Not Suppressed
2.20 %	0.38 grams	Fire Not Suppressed
3.85 %	0.67 grams	Fire Not Suppressed
3.85 %	0.67 grams	Fire Suppressed
3.85 %	0.67 grams	Fire Not Suppressed
5.89 %	1.03 grams	Fire Suppressed
10.0 %	1.75 grams	Fire Suppressed
41.0 %	7.16 grams	Fire Suppressed
50.0 %	8.73 grams	Fire Suppressed

Results Using Solid-Solid Hybrid Gas Generators

A total of 10 solid-solid hybrid gas generators were procured for testing on this effort. They all contained 20 grams of non-azide formulation #1 and 50 grams of octabromodiphenyl oxide, which will generate 17.5 grams of inert gas and 26.7 grams of bromide gas, or a total of 44.6 grams of gas (the amount of bromide gas is based on earlier bromide analysis). For the experiments, the air flow was set to 12.1 miles per hour (5.4 m/s) and the propane flow was set at 85 ml/s. These are the same flow conditions that NIST used in the TARPF apparatus when testing gas generators.

Table 5 presents the test results for the solid-solid hybrid gas generators. The mass of gas supplied to TARPF is the total amount of gas generated (44.6 grams for the solid-solid hybrid gas generators) multiplied by the % open area to TARPF (the remaining gas goes to the bypass stream). Table 6 shows that 0.44 grams of hybrid agent gas put out the fire 0 % of the time and 0.98 grams of hybrid agent gas suppressed the fire 100 % of the time. More tests between the 0.44 and 0.98 gram level need to be performed to more fully determine what percentage of the fires could be suppressed versus the amount of gas supplied. Unfortunately, timing and funding limitations prevented procurement and testing of additional gas generators.

Table 5 – TARPF Test Results for Solid-Solid Hybrid Gas Generators

% Open Area to TARPF	Mass of Gas to TARPF	Result
0.99 %	0.44 grams	Fire Not Suppressed
0.99 %	0.44 grams	Fire Not Suppressed
0.99 %	0.44 grams	Fire Not Suppressed
2.20 %	0.98 grams	Fire Suppressed
2.20 %	0.98 grams	Fire Suppressed
2.20 %	0.98 grams	Fire Suppressed
3.85 %	1.72 grams	Fire Suppressed

Comparison of Conventional and Solid-Solid Hybrid Gas Generators

It is difficult from the data presented in Tables 4 and 5 to differentiate the performance between the conventional and solid-solid hybrid gas generators. More data would be required to fully determine the difference in their performance. Another reason for the difficulty in differentiating their performance is due to the scale of the TARPF facility relative to the amount of gas supplied by the generators. With only approximately 2-5 % of the gas that is generated required for suppression, and roughly 95-98% of the gas bypassed, the error in the calculation of the mass of gas supplied to TARPF is quite large, making the data have a wide error band. A larger-scale apparatus would allow for a more accurate comparison of the performance of the two gas generator configurations.

CONCLUSIONS

The technical objectives of this effort were to evaluate and select improved inert gas generator (propellant) formulations, to package the propellant with the flame retardant inside the same housing, to evaluate various solid-solid hybrid system variables and select an optimum configuration that maximizes system performance, and to perform larger-scale fire suppression tests with the optimum configuration. Each of the objectives was successfully met.

Three propellant formulations were evaluated, one azide and two non-azide formulations. The azide formulation and non-azide formulation #2 were ineffective at fire suppression in the cup burner. Therefore, azide formulation #1 was selected for future work. A prototype housing configuration was developed that contained 20 grams of propellant and varying amounts of flame retardant. Experiments were performed to optimize the performance of the solid-solid hybrid gas generator using the housing configuration and the inert gas generator selected. The following experimental variables were examined: flame retardant type and the ratio of propellant to flame retardant. The experimental results that were used to determine the optimum conditions are minimizing cup burner FEC and maximizing the amount of bromine and bromide ion formation. The optimized configuration consisted of 20 grams of TAL-1308 with 50 grams of octabromodiphenyl oxide.

Larger-scale fire suppression experiments were performed in a transient application, recirculating pool fire (TARPF) apparatus fabricated at Mainstream. Mainstream's TARPF was designed with features and dimensions as close to the NIST TARPF as possible, with only minor exceptions. Both conventional gas generators and the solid-solid hybrid gas generators were tested. Both types of gas generators were successful at extinguishment when about 1 gram of agent was supplied to the fire. It was difficult to differentiate the performance between the conventional and solid-solid hybrid gas generators. More data would be required to fully determine the difference in their performance. Another reason for the difficulty in differentiating their performance is due to the scale of the TARPF facility relative to the amount of gas supplied by the generators. With only a small fraction of the gas that is generated required for suppression, and most of the gas bypassed, the error in the calculation of the mass of gas supplied to TARPF is quite large, making the data have a wide error band. A larger-scale apparatus would allow for a more accurate comparison of the performance of the two gas generator configurations.

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