THERMODYNAMIC DESIGN OF AN ALTERNATIVE MONOPROPELLANT FOR EMERGENCY POWER UNITS

Shin Matsumura, John J. Rusek
Department of Aeronautics and Astronautics
Purdue University
West Lafayette, IN 47906 USA

Keywords: *Hydrogen Peroxide, Monopropellant, Emergency Power Units*

Abstract

A monopropellant to replace hydrazine in emergency power units used in military aircraft has been formulated from a thermodynamic design approach. The combustion products from a combined mixture of hydrogen peroxide and a miscible organic fuel have shown that the energy available far exceeds that of pure hydrogen peroxide or of hydrazine.

The propellant mixture was analyzed and formulated using a thermochemistry code and the simplex downhill method for the optimization of a design objective function. The results have shown that even with the most common fuels such as methanol, acetaldehyde, acetonitrile, acetone, and methyl ethyl ketone, a decrease of about a factor of two in the propellant volume, or an increase of about a factor two in the total operation time is possible. This is primarily due to the high concentration of methane gas in the product species resulting in a high specific heat.

Kinetic tests were then performed for various mixture ratios for selected fuels to determine whether the designed formulations can be auto-ignited from the heat given off from the decomposition of peroxide. Sodium promoted manganese dioxide impregnated on a cordierite ceramic block was used as the combustion catalyst. The results showed that the mixture ratios that can be auto-ignited when using this catalyst was bound to a region within about 30 % of stoichiometric mixture ratios.

1 Introduction

Recently, there has been an increase in attention for replacing highly toxic chemical energy sources such as hydrazine used in chemical rockets and emergency power units (EPU). With the limited supply of natural fuel left around the world, a nontoxic, inexpensive chemical energy source is highly in demand. Not only will such technology be useful for aerospace applications, and there are potential uses in commercial fields such as automobiles, household appliances, portable electronics, etc.

Hydrogen peroxide (HP) has long been known to be a useful energy source. During World War II, the Germans experimented and later developed rockets, underwater craft, and aircraft powered with HP [1]. Recently, Beal Aerospace Corporation successfully test fired a HP powered second stage booster rocket with over 500,000 pounds of thrust [2].

In EPU's that use hydrazine, the propellant is run through a catalyst bed for decomposition. The resulting high temperature gas is then fed into a turbine for power generation. A study was done using 70 % HP as a replacement propellant for an EPU, in an attempt to eliminate the highly toxic hydrazine [3]. 70 % HP would be much safer and cleaner than hydrazine, however it has been shown that there is some penalty in the performance of the EPU.

A concept to improve the performance of HP based monopropellant is to mix HP and some organic fuel as a monopropellant, and to use the heat released from the decomposition of HP for combustion. This is different from current power systems that use HP and fuel, in that in current systems, the two liquids are stored separately, and are injected into the combustion chamber for decomposition and/or ignition. This allows for more energetic fuels and fuels that are hypergolic with HP, but with a penalty of a more complex system, requiring two propellant tanks, feed systems, and so on. Pre-mixing the HP and the fuel can be beneficial for size-limited systems such as EPU's, with the added benefit of no need for an igniter for this application.

A thermodynamic design and analysis was done with various organic fuels, with several design constraints to avoid detonations, chemical incompatibilities, etc. The kinetics of the propellants was then tested with drop tests, to determine whether the heat released from the HP decomposition can be used as the ignition source. This paper will discuss the formulation design of this HP-based monopropellant, estimated performance of an EPU using this propellant, and the results of the drop tests.

2 Optimization and Thermodynamic Analysis Routine

As with most designs, iteration methods are necessary. This work implemented the downhill simplex method from [4], so that the design could be automated. The simplex method was chosen due to the simplicity of the algorithm, and because it uses only the values of the function evaluated and not the derivatives for the iteration. This makes the method inefficient in terms of the number of function evaluations it must perform, but offers the advantage of global optimization.

Using this method for propellant formulation optimization, the independent variables were the mass percentage of HP and the fuel, and the function to be minimized was an objective function specified by the design target. The mass percentage of water is automatically determined from the above information. More discussion on the objective function and its development will be given later.

The analysis of the propellant was done purely from a thermodynamic point of view. The performance of the EPU as a system was analyzed after the propellants were formulated. In general, it is often "better" to simultaneously design the entire system when using an optimization routine. In this case however, it was thought that if only the propellant could be replaced and everything else kept the same, then the development and modification cost of the EPU could be reduced.

A thermochemistry computer code developed by NASA Lewis Research Center [5] was used to compute the necessary parameters of the combustion process such as flame temperature, specific heat, etc. Equilibrium flow was assumed, and the combustion pressure was kept the same as that of a baseline test case.

3 Design Space, Constraints, and Bounds

The design space consists of only two variables, percentage of HP and fuel by weight. Although these are continuous variables, there are definite bounds. Figure 1 shows the formulation design space. The detonation limit is shown in red. Sources such as [1] and [6] report that for certain mixture ratios of HP and organic fuel, the fuel acts as a catalyst for the decomposition of HP, and can cause the mixture to detonate. This boundary is unique for the type of fuel used, and due to the limited experimental data available, the most conservative limit, which was for acetone, was used for all fuels considered.

With mixtures consisting of only HP and water, the heat released from the decomposition of HP using a catalyst evaporates the water. Under adiabatic conditions, this is possible down to HP strength of about 68 % [1]. A slightly conservative value of 70 % was used instead, and was extended into the design space. This is the second boundary, shown in green. The idea was that for mixture ratios to the right of this line, the mixture has too much water and/or fuel, and the propellant will not auto-

ignite. The formulation triangle, detonation limit, and the auto-ignition limit narrow the design space down to the upper rhombus-like region. However it is still important to explore the performance of the propellant outside of this region, and will be done.

There is also a maximum flame temperature constraint on the formulation design, because there is a limit on the turbine inlet temperature. The maximum turbine inlet temperature for typical turbines for this application was used for the maximum adiabatic flame temperature.

The simplex method can now be used within this region to find the optimum mixture ratio, which will be defined later. An overview of the types of fuels considered will be given next, along with the reasons for eliminating some of them.

4 Types of Fuels Considered

There is really another design variable, which is the type of fuel to be used. This however is not something that can be incorporated with the simplex method, because this variable only has discrete values. Initially, a list of possible fuels were made, and the most promising fuels were chosen based on qualitative considerations such as compatibility with HP and toxicity. These fuels and their characteristics were obtained from chemistry handbooks such as [7], [8], and [9]. A listing of these 30 initial fuels, and the reasons for eliminating some of them is shown in Table 1.

With the remaining 14 possible fuels, the thermochemistry code was used to predict some of the fundamental thermodynamic characteristics, such as flame temperature. The results showed that acetic acid, formic acid, glycerol, and nitromethane has too high of a flame temperature for the turbine on the EPU. Six fuels, methanol, acetadehyde, acetonitrile, acetone, methyl ethyl ketone, and formamide were chosen for a more detailed analysis. The mixtures for each of these fuels were optimized based on an objective function that characterize the performance of the fuels, but directly translate into the system performance, and were ranked accordingly. The formulation of the objective function for the optimization will be given next.

5 Design Objective Function

The objective function must be a characterization only of the propellant, but must also somehow predict the system performance of the EPU. This is for the reason mentioned earlier, in that in the ideal case only the propellant would be replaced and the remainder of the existing EPU's would be the same.

The enthalpy flow rate, or the amount of energy flowing into the EPU turbine per unit of time is given below in Equation 1.

$$\dot{h} = \dot{m} CpT \tag{1}$$

Here, $\dot{m}$ is the mass flow rate, C_p is the specific heat at constant pressure, and T is the temperature of the gas. If the combusted gas of the new propellant is to provide the same amount of power to the turbine, then the enthalpy flow rate must match that of the current system, shown in Equation 2.

$$\dot{m} CpT = \dot{h}_{ref} \tag{2}$$

The subscript "*ref*" is used to denote the reference value, which is the value for the current system. The reference enthalpy flow rate is presumed to be known, or can be calculated [3]. Equation 2 can be rearranged to provide an equation that relates the volume of the propellant to the total operation time of the EPU, assuming a constant mass flow rate, shown in Equation 3.

$$t = V \frac{\rho CpT}{\dot{h}_{ref}} \tag{3}$$

Here, t is the operation time, V is the volume of the propellant, and ρ is the density of the propellant. This equation states that if the volume of the propellant tank is kept the same as the current EPU and ρCpT of the new

propellant is greater than the enthalpy flow rate of hydrazine, then a longer operation time is possible. Conversely, if the operation time is kept the same, then less fuel is needed. Equation 3 predicts the performance of the EPU system with the parameter ρCpT, which depends solely on the propellant formulation.

The quantity ρCpT appears to be the enthalpy per unit volume flowing into the turbine, however very subtly it is not, because the density here is for the propellant, and CpT is the specific enthalpy of the combusted gas. This parameter was identified as the value to maximize using the optimization routine, with penalty functions to keep the propellant formulation within the boundaries. The objective function I used is shown below in Equation 4.

$$I = \left[1 + \frac{\dot{h}_{ref}}{\rho CpT}\right]^2 + z\left[\frac{|T_{\max} - T|}{T_{\max}}\right]^2 \qquad (4)$$

The second term is the penalty function to force the optimization to a formulation that will result in a flame temperature equal to the maximum turbine inlet temperature. z is the penalty factor and T_{max} is the maximum turbine inlet temperature.

6 Results of Optimization and Analysis

The optimized values of the three propellant component fractions and the resulting ρCpT for the six fuels are listed in Table 2. Table 3 lists the same parameters for hydrazine, two concentrations of HP, and only the fuels, for comparison. The two approximations for hydrazine is from the new propellant's point of view, in that a conservative approximation will give a high value of ρCpT for hydrazine. The table shows that 70 % HP is inferior by a factor of about 2, compared to the liberal approximation of hydrazine, and 85.5 % strength would be needed to match hydrazine. It is not possible to react only the fuel, but this was done to see that there is a benefit by mixing HP and fuel. All six of the fuels resulted in a ρCpT greater than the conservative approximation for hydrazine by a factor of about two. The optimized formulations are shown in the formulation triangle in Figure 2. A problem can immediately be seen, in that the design points for each fuel lie very close, or on the boundaries. This happens because of the maximum temperature limit and of the local ρCpT maximum, which will be discussed next. This also motivates the need for performing detonation and decomposition experiments, in order to define the boundaries as accurately as possible for each fuel of interest.

An analysis of methanol will be presented to explore the behavior of the objective function inside the complete formulation triangle. The thermodynamic quantities such as flame temperature, specific heat, and product species will be explored, to investigate how they change as the mixture ratio changes. A contour of the flame temperature is shown in Figure 3. The maximum temperature occurs at the stoichiometric mixture ratio, and the temperature decreases almost symmetrically as the mixture becomes fuel rich or lean. Figure 4 shows a contour of ρCpT. The stoichiometric line is again visible, but there is a local maximum near the design point. The contour of specific heat, shown in Figure 5, shows where the local maximum of ρCpT comes from. This plot has a similar pattern to Figure 4, with two local maximums. However, the global maximum for the specific heat is near the design point, not at the stoichiometric mixture ratio. The physical reason for this high specific heat can be explained by comparing the type and amount of product species from combustion. This is listed in Table 4 along with the specific heat for three mixture ratios, stoichiometric, local maximum of ρCpT, and the design point. The high specific heats are probably caused by the large amounts of methane gas, which is formed when the mixture is fuel rich.

As for the five other fuels, even though the locations of the ρCpT local maximum, maximum specific heat, etc. differed slightly, they all had the same trends as methanol. A possible problem that could arise is that the

methane gas present in the combusted gas may cause complications with the turbine. According to [3] however, the turbines should be able to handle modest amounts of soot and burnt hydrocarbons. Nevertheless, this should be addressed in the future.

7 EPU System Performance Using HP/Methanol

Using the optimized value of ρCpT, the relationship between the operation time and the propellant volume can be plotted, shown in Figure 6. This was done using both the conservative and liberal approximations for the reference enthalpy flow rate. Once again, "conservative" and "liberal" is from the new propellant's point of view, in that a small ρCpT for hydrazine is liberal because it favors the new propellant. It can be expected that the actual performance will be somewhere in between these two approximations. Two plots for HP are also shown for comparison. ρCpT for 70 % HP is so much lower than hydrazine that the same volume of propellant as the baseline would result in a much shorter operation time.

The results for the new propellants show that even with the conservative approximation for the current system, if the operation time is kept the same, then the amount of propellant can be reduced by 50 %. If the volume of propellant is kept the same, then the operation time can be doubled. Either of these would be a significant improvement, and may be of interest for the EPU's on the next-generation military aircraft such as Unmanned Air Vehicles (UAV), the F-22 Raptor, and the Joint Strike Fighter (JSF). Because these aircraft are not in full production or service yet, it is possible to investigate the effect of decreasing the size of the EPU on the aircraft performance. For aircraft currently in service however, replacing only the propellant and increasing the operation time may be the better choice.

8 Experimental Setup and Results

Drop tests of the new propellant at various mixture ratios were done to determine the actual auto-ignition boundary, which was assumed during the numerical design. The test consisted of mixing HP and fuel to the desired mixture ratio, and then using a pipette to drop it on a catalyst block. The catalyst used was sodium permanganate, impregnated on a cordierite ceramic block.

A total of five alcohols, acetone, methyl ethyl ketone (MEK), methanol, ethanol, and propanol were tested. Although ethanol and propanol were not numerically analyzed, they were tested because they are readily available, well-known fuels. For the first three fuels, the design points were first tested. The result was that there was not enough heat to vaporize all of the propellant, and the liquid propellant sizzled on the catalyst block when dropped. The design mixture ratios were modified by slightly increasing the amount of HP, however all of these tests also had the same problem.

The mixture ratio was then shifted much closer to stoichiometric, to explore the region within the detonation range. Although there was a danger of detonation during the mixing process, this was thought to be highly unlikely, because [1] and [6] report that devices such as blasting caps and impact testers were used. Various mixture ratios were tested, to experimentally determine what mixture ratio ranges can be auto-ignited.

The results of the drop tests for the five fuels are shown in Figures 7-11. The experimentally derived auto-ignition boundary is shown in green. The data suggests that the mixture must be well within the published detonation region to achieve auto-ignition, which is a discouraging result. However, there is also the possibility of scaling effects. By testing only a drop of the monopropellant at a time, a fraction of the heat available for ignition is lost to the surrounding and to the catalyst block, although the exact percentage of lost heat is unknown. With a flow test, using a catalyst block preheated to the operating temperature, the auto-ignition region might be expanded. Another possibility is to use a different catalyst. For these tests, the molar ratio of sodium to manganese for the catalyst was one to one. Changing the ratio may

result in a more efficient decomposition of HP, providing more energy for ignition.

Despite these possibilities, an attempt was made to find a correlation of the auto-ignition region using different fuels to some physical property of the monopropellant. It seemed logical that the monopropellant with the "easiest" fuel to ignite would have a larger auto-ignition region. The flash point and auto-ignition temperature from [10] was compared against the sizes of the areas, and the results are tabulated in Table 5. A correlation can be seen with the flash point, in that the fuel with the lowest flash point has the largest auto-ignition region. Ethanol and methanol seems to be reversed in their orders, however there is also the possibility of experimental error. These include the scaling effects discussed previously, and also the auto-ignition regions were data-fitted after the drop tests were performed. With small areas such as with these fuels, there is a high possibility of uncertainty.

9 Summary

A monopropellant to replace hydrazine in EPU's has been designed. The concept of the design is to mix HP and some miscible organic fuel as a monopropellant. This has problems, the most serious being the fuel acting as a catalyst for the HP decomposition and causing the propellant to detonate. This was taken into account using the detonation limit for acetone, and assuming that it could be applicable to the fuels considered.

The design was done numerically, and the parameter ρCpT was maximized using an optimization routine, with the constraint that the flame temperature could not exceed the maximum turbine inlet temperature, and that the formulation had to be within the detonation and auto-ignition boundaries. The parameter ρCpT was derived from the statement that the enthalpy flow rate into the turbine must be equal to that of the current system. The parameter was useful because it depended only on the thermodynamics of the chemical reaction, but predicted the EPU system performance.

Using the optimized formulations, it was found that the current system could be significantly improved. If the operation time was kept the same as the current system, then the volume of propellant required could be reduced by 50 %. If the volume of the propellant was kept the same, the operation time could be doubled.

Drop tests showed a possible correlation between the sizes of the auto-ignition region to the flash point of the fuels used. The optimized formulations were well outside of the experimentally derived auto-ignition region, however there is the possibility of scaling effects, and of using a more efficient catalyst for HP decomposition.

Acknowledgements

The authors would like to express special thanks to propulsion faculty member Dr. Stephen Heister at Purdue University and Angel Gonzalez of Lockheed Martin Skunkworks for their advice and expertise they provided, and graduate student Trisha Beutien for the manufacture of the catalyst blocks.

References

[1] C. N. Satterfield, W. C. Schumb, and R. L. Wentworth. Hydrogen Peroxide. Reinhold Publishing Corporation Copyright 1955. New York

[2] Beal Aerospace News Fact Sheet: The BA-810 Rocket Engine. Beal Aerospace Corporation

[3] A. M. Gonzalez. ESS Study for H-70 and H_2O_2. Lockheed Martin Corporation

[4] B. Flannery, W. Press, S. Teukolsky, W. Vetterling. Numerical Recipes in FORTRAN 2nd Ed. Cambridge University Press Copyright 1992

[5] S. Gordon and B. J. McBride. Computer Program for Calculation of Complex

Chemical Equilibrium Composition, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouget Detonations. NASA Lewis Research Center SP- 273, 1971

[6] D. C. Lehwalder, J. M. Monger, and H. Sello. "Explosion Limits of Liquid Systems Containing Hydrogen Peroxide, Water, and Oxygenated Organic Compounds," *Journal of Chemical and Engineering Data*. January 1961 Vol. 6 No. 1

[7] D. W. Green and R. H. Perry. Perry's Chemical Engineer's Handbook 7th Ed. McGraw-Hill Copyright 1997 New York

[8] D R. Lide, Editor. CRC Handbook of Chemistry and Physics 75th Ed. CRC Press Copyright 1994 Ann Arbor

[9] P. G. Stecher, Editor. The Merck Index 8th Ed. Merck & Co., Inc. Copyright 1968 Rahway

[10] Materials Safety Data Sheets. http://www.jtbaker.com. Mallinckrodt Baker Inc. Copyright 1997-2000

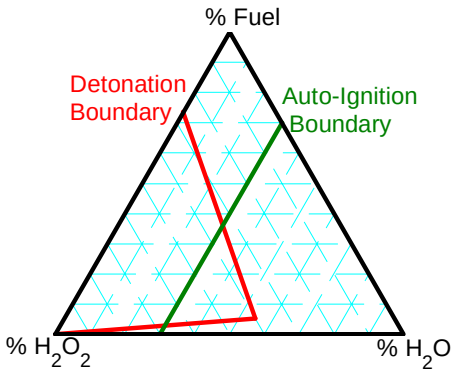

Fig.1. Formulation Triangle and Design Space

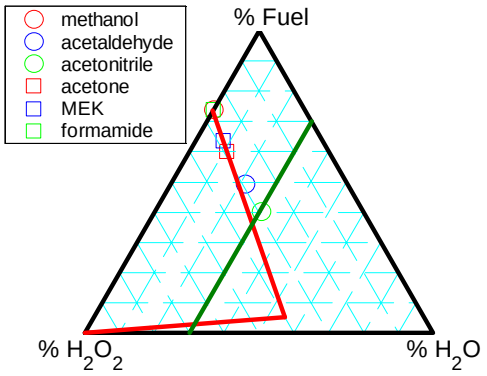

Fig.2. Optimized Mixture Ratios

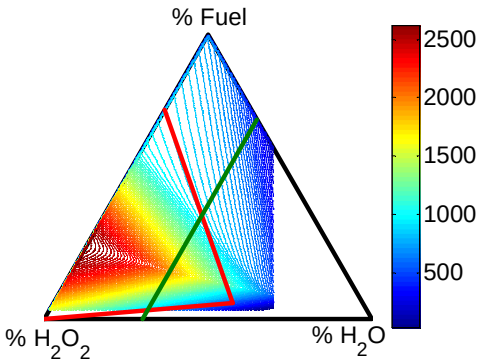

Fig.3. Flame Temperature (K) for HP/Methanol

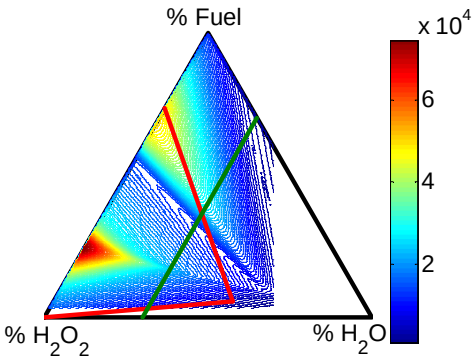

Fig.4. ρCpT (cal/in^3) for HP/Methanol

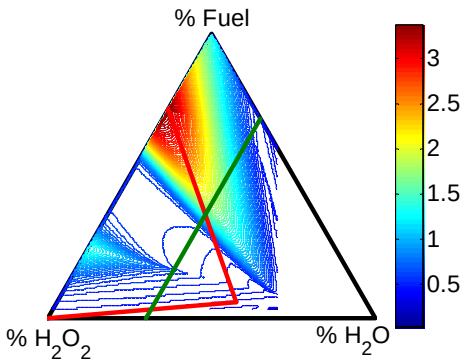

Fig.5. Specific Heat (cal/g-K) for HP/Methanol

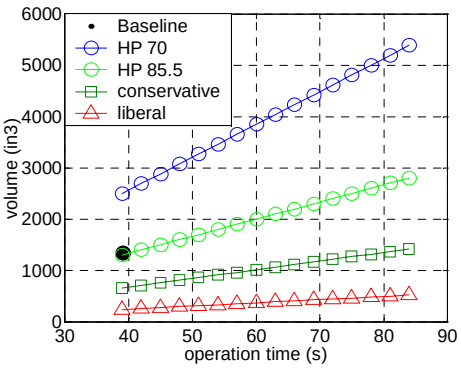

Fig.6. Operation Time and Propellant Volume for HP/Methanol

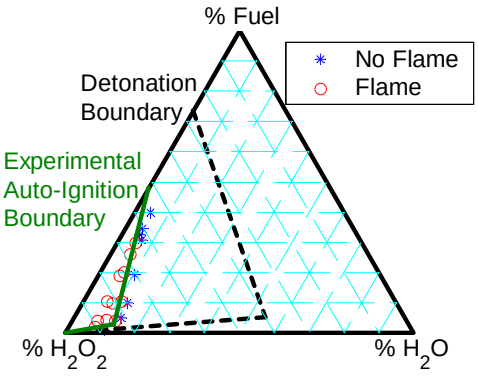

Fig.7. Drop Test Results for HP/Acetone

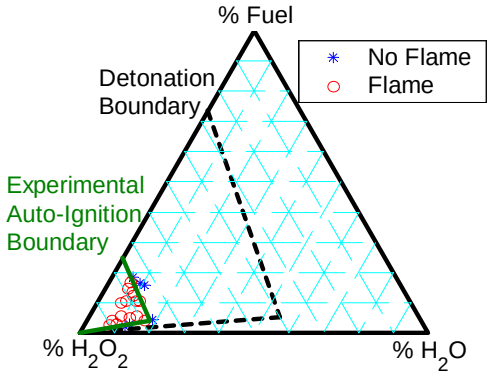

Fig.8. Drop Test Results for HP/MEK

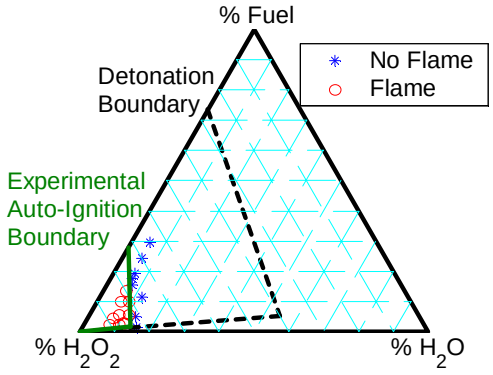

Fig.9. Drop Test Results for HP/Ethanol

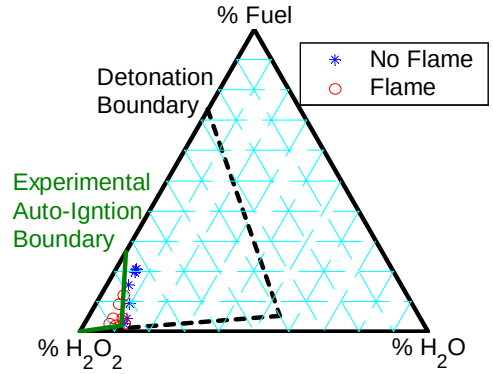

Fig.10. Drop Test Results for HP/Propanol

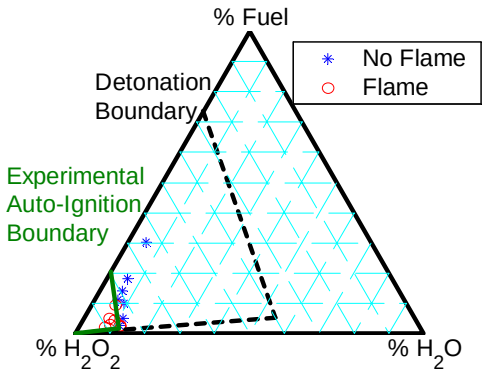

Fig.11. Drop Test Results for HP/Methanol

Table.1. Listing of the Initial 30 Possible Fuels

FUEL	PROBLEM		FUEL	PROBLEM
Methyl Ethyl Ketone	NONE		Glycerol	NONE
Acetaldehyde	NONE		Heptane	Gaseous
Acetic Acid	NONE		Heptanol	Insoluble in HP
Acetonitrile	NONE		Methanol	NONE
Acetone	NONE		Methyl Acetate	NONE
Butane	Gaseous		Methylamine	Toxic
Diethyl Ether	Explosive w/ HP		Nitromethane	NONE
Divinyl Ether	Explosive w/ HP		Pentane	Insoluble in HP
Ethane	Gaseous		Phenol	Toxic
Ethanol	NONE		Propane	Gaseous
Ethylene Oxide	NONE		Propanol	NONE
Formaldehyde	Gaseous		Propionaldehyde	Explosive w/ HP
Formamide	NONE		Tetrahydrofuran	Explosive w/ HP
Formic Acid	NONE		Urea	NONE
Furan	Explosive w/ HP		Vinyl Acetate	Insoluble in HP

Table.2. Weight Breakdown of Fuel and HP at Optimized Mixture Ratio Using Each Fuel, and Performance Parameter

Fuel	% Fuel	% HP	ρCpT (cal/in^3)
Methanol	73.76	26.24	46387
Acetaldehyde	49.32	29.26	46019
Acetonitrile	40.14	29.28	43515
Acetone	60.05	29.13	42983
Methyl Ethyl Ketone	63.60	28.44	42383
Formamide	73.48	26.52	38531

Table.3. Thermodynamic Quantities and Performance Parameter for Hydrazine, HP, and Fuels

Propellant	ρCpT (cal/in^3)
Hydrazine (conservative)	22967
Hydrazine (liberal)	8697
70 % HP	4485
85.5 % HP	8618
Methanol	12905
Acetaldehyde	24045
89% Acetonitrile	22321
Acetone	12215
Methyl Ethyl Ketone	11671
Formamide	2846

Table.4. Mole Fractions of the Product Species and Thermodynamic Quantities for HP/Methanol

	CO	CO_2	H_2	H_2O	O_2	CH_4	OH	Cp (cal/g-K)
Stoichiometric	0.034	0.128	0.030	0.756	0.021	0.000	0.025	1.3753
Secondary	0.121	0.134	0.408	0.249	0.000	0.089	0.000	3.2649
Design	0.102	0.144	0.369	0.249	0.000	0.137	0.000	3.2913

Table.5. Comparison of Experimental Auto-Ignition Region Size to Physical Properties of the Fuels

Fuel	Auto-Ignition Region Area (% of Total Triangle)	Auto-Ignition Temperature (˚C)	Flash Point (˚C)
Acetone	12.287	465	-20
Methyl Ethyl Ketone	8.821	404	-9
Ethanol	7.573	463	13
Propanol	5.713	399	12
Methanol	4.522	464	11