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Parameters Influencing Regression Rate of Solid Rocket Fuels

Review Article

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Abstract

This review paper provides a compilation of works from 1966 to 2018 pertaining to the study of altering the burn rate for solid fuel rockets. This paper serves to catalog the current state of research on burn rate altering additives and other common methods for tailoring the burn rate of solid rocket fuels for specific applications. Solid rocket motors (SRM) and hybrid rocket engines (HRE) both utilize solid fuels, while SRMs use a solid oxidizer mixed into the fuel and HREs use liquid or gas oxidizer separated from the fuel. There are many different methods for controlling the burn rate of these motors and engines, such as: fuel and oxidizer choice and concentration, additives, grain configuration, and combustion chamber pressure. The methods for controlling burn rate for each particular rocket type are discussed in their own sections, however most additives that mix with the solid fuel remain the same across the SRMs and HREs with the exception of those that behave as oxidizers. The main goal of this study of the modification, not just increasing, of the burn rate for these fuels is their use in long distance unmanned aerial vehicle (UAV) applications. HREs have many benefits that make them ideal for UAVs, including: low cost, added safety and ease of storage, and low burn rate. HRE have the added benefit of increased safety due to the physical separation of the fuel and oxidizer, and any additives that release oxygen during decomposition would not be ideal. Additives are a key element discussed in this paper, as the concentration can be varied to precisely tailor the burn rate of a mixture. The additives alter the burn rate by influencing the activation energy, heat of reaction, and efficiency of energy feedback.

Keywords: Burn Rate Modification; Solid Rocket Motors; Hybrid Rocket Engines; Propellant Additives, UAV.

Abbreviations: SRM: Solid Rocket Motors; HRE: Hybrid Rocket Engines; UAV: Unmanned Aerial Vehicle; LRE: Liquid Rocket Engine; AP: Ammonium Perchlorate; HTBP: Hydroxyl-Terminated Polybutadiene; ABS: Acrylonitrile Butadiene Styrene; GOX: Gaseous Oxygen; NOX: Nitrous Oxide; TAGzT: Triaminoguanidinium Azotetrazolate.

Introduction

This review is about solid rocket propellants and how to customize their burning rates for applications that require long time/range thrust operations. Rockets can be divided into different categories based on the states of matter their oxidizers and fuel are in. Figure 1 illustrates the breakdown of the different classifications of rockets. Rockets that utilize a solid fuel mixed with a solid oxidizer are referred to as solid rocket motors (SRM). These motors are commonly used as boosters for spacecraft launches or other long-range payloads. Compared to their liquid rocket engine (LRE) counterparts that utilize both liquid fuel and liquid oxidizer, SRMs are less complex but are also more dangerous. With the fuel and oxidizer already premixed in SRM, once the propellant mixture is ignited, the burning continues to propagate and cannot be shut off easily. SRMs also have increased sensitivity to accidental ignition and must be stored and transported safely, this leads to an increase in cost. Liquid rocket engines separate the fuel and oxidizer while having the ability to throttle the fuel and oxidizer mixture ratio, providing thrust adjustability and additional safety but also increasing complexity by having pumps and multiple injectors. Hybrid rocket engines (HRE) offer the safety benefits of liquid rocket engines by separating the fuel and oxidizer while also having some of the benefits of solid rocket motors in terms of

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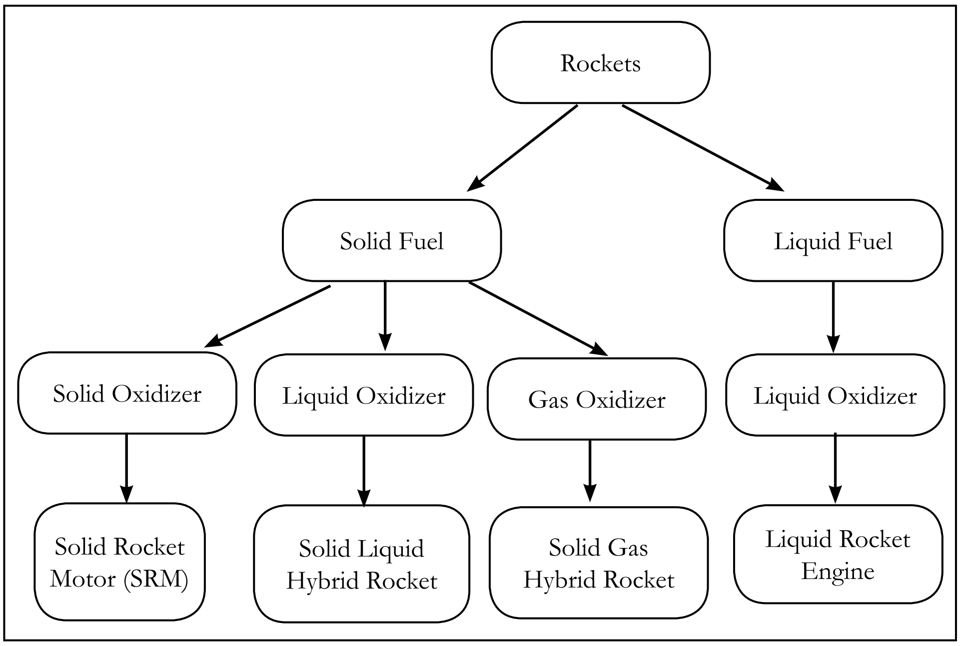
Figure 1. Classification of rockets from propellant states.



the simplicity and performance.

The hybrid rocket engines discussed in this paper are the solid fuel hybrid engines. There exists liquid or gas fuel with solid oxidizer hybrid rockets, commonly referred to as reverse hybrid engines, but the most popular hybrid engines are those that utilize a solid fuel and either a liquid or gaseous oxidizer. The focus of this paper is to compile the various methods of altering the burn rate for rockets composed of solid fuel with a centralized focus on hybrid rocket engines. HREs are more ideal for UAV applications, for reasons that will be discussed in detail in later sections. Burn rate determines the rate of energy release, and the flame temperature. The linear burning rate, or regression rate, of a propellant is usually measured in mm/sec while the mass burning rate of a propellant is measured in g/sec. There are many factors that can influence the regression rate for each type of rocket fuel and each section will list several of them. However, the focus of the paper is to evaluate the regression rate of several common propellant mixtures combined with common regression rate modifying additives. Propellant additives are chemicals that are added to the mixture that do not have the primary role as a fuel, oxidizer, binder, or cross-link agent.

Modifications for Solid Rocket Motor Regression Rate

The regression rate of most composite (discussed in later sections) SRM propellants can be expressed using St. Robert's Law:

$$r = r_o + aP_c^n$$

where r is the regression rate, r_o is a constant (usually taken as zero), a is the regression rate coefficient, and n is the pressure exponent, P_c is the pressure of the combustion chamber. The values of a and n are determined empirically for each propellant formulation. On log-log scales, the relationship between chamber pressure and regression rate is linear for propellant that obeys St. Robert's Law. However, for propellants that do not obey this equation, the slope of the relationship might not be constant for all pressures due to the influence of additional variables as explained in [20] through experimental data. For the two limits of n=1, and n=0, the regression rate changes from linear relationship to constant value respectively. To relate the erosive burning rate to the gas flow in the combustion chamber, various empirical laws are used:

$$r = aP_c^n[1 + k(G - G^*)] \quad \textit{multiplicative law}$$

where k is a constant, and G is the specific mass flow rate of the main flow, and G* is a threshold flow rate.

$$r = aP_c^n + ku \quad \textit{additive law}$$

where k is a constant, and u is the velocity of the main flow.

There are many different factors that influence the regression rate of a mixed fuel and oxidizer propellant; several examples of the most influential factors are provided in Table 1.

There are many more factors that control regression rate beyond what is listed in Table 1, for example, Control of Pyrotechnic Burn Rate [23] lists up to 15 methods. The burning rate differs significantly between different fuels and oxidizers while the addition of additives in small fractions of the total mixture can precisely tailor the mixture to achieve the desired burning rate.

Choice of Fuel and Oxidizer for SRM

The main SRM propellant type being reviewed in this section is a composite type which consists of separate fuel, oxidizer, binding agent, and additives all mixed together. The other type of solid propellant is referred to as "double base propellants" which contain nitrocellulose and nitroglycerine; both of which are oxyhydrocarbons, meaning they each contain the fuel and oxygen necessary for combustion.

Composite propellants that utilize metal fuels typically have a higher regression rate due to the amount high amount of heat given off during their exothermic combustion as well as having high thermal conductivity values, meaning the temperature increase can penetrate deeper into fuel grain. This increase in temperature corresponds to an increase in energy of the mixture prior to combustion, therefore, there is less energy required to reach the activation energy necessary for the combustion reaction to occur. Space Propulsion Analysis and Design [20] outlines a list of solid metal fuels organized by their efficiency of combustion. Control of Pyrotechnic Burn Rate [23] summarizes several fuels and their heat of combustion, which is how much heat energy they put back into the system for further combustion. Aluminum powder is on the higher end of the spectrum with 7400 cal/g and Sulfur is on the low end with 2200 cal/g.

Oxidizers also vary in their decomposition temperature, which is the temperature required for reactants to form, and by the amount of heat released after combustion. The lower the decomposition temperature and the higher amount of energy released after combustion, the faster the regression rate of the propellant. The mass percentage of oxygen in the molecule of the oxidizer is also a good indicator of performance. A common oxidizer molecule such as Ammonium Perchlorate (AP) has a chemical formula NH_4ClO_4 which results in 59.5% of the molecular weight coming from the oxygen molecules. Another common oxidizer, Potassium Nitrate (KNO_3), has a lower performance compared to AP, partly due to the lower mass percentage of oxygen at 47.5%. Another aspect of regression rate comes from the strength between the bonds of the reactants (fuel and oxidizer) and products (chemicals formed after combustion). Usually the stronger the bonds are in the products relative to the bonds in reactants, the greater the net generation of heat from combustion. KNO_3 also has an endothermic decomposition, which means it will it will take more energy to decompose than the amount of energy given off by the formation of its products. Thus, to provide a net positive heat generation to the fuel grain to keep burning, a fuel or additives must be used that release more energy on combustion than is required by the amount of KNO_3 in the mixture.

Table 1. List of common factors that control the regression rate of solid rocket propellant.

Method	References
1. Choice of fuel and oxidizer	[14, 20, 23, 40]
2. Fuel to oxidizer ratio	[14, 23, 40]
3. Ambient propellant temperature	[14, 20, 23, 30, 40]
4. Combustion chamber pressure	[14, 30, 40]
5. The presence of additives or catalysts	[14, 20, 23, 40]

Table 2. Common additives for suppressing regression rate of SRMs.

Additive	References
Calcium Carbonate	[14, 40]
Magnesium Carbonate	[14, 40]
Barium Carbonate	[23]
Strontium Carbonate	[23]
Sodium Bicarbonate	[14, 23, 40]
Clay	[14]
Diatomaceous earth	[14]
Lithium Fluoride	[9, 40]

Table 3. Common additives for accelerating regression rate of SRMs.

Additive	References
Wires or metal staples	[40]
Iron Oxide*	[9, 14, 20, 23, 28, 40]
Copper Oxide	[37, 40]
Molybdenum Oxide	[37]
Zirconium Oxide	[23, 37]
Potassium Dichromate*	[23]
Manganese Dioxide*	[23]
Lead Stearate	[40]

*Denotes common catalyst additives

Additives for SRM Propellant

Additives can be used to precisely control the burn rate of a fuel mixture through altering the additives concentration. Burn rate retardant additives usually work by increasing the activation energy of a mixture, by having an endothermic decomposition reaction, or both. Catalysts work by lowering the activation energy required for the decomposition of the oxidizer, which releases more oxygen to use for combustion of the fuels. Unlike other additives, catalysts are not typically consumed in the reaction.

Modifications for Hybrid Rocket Engine Solid Fuel Regression Rate

Hybrid rocket engines have been known to have comparably low regression rates to their SRM counterparts. Much work has been done finding methods of increasing the burn rate or thrust output for HREs. Since the fuel and oxidizer are not already mixed like in SRMs, the regression rate of the solid fuel in a HRE is dependent on the amount of liquid oxidizer being put into the combustion chamber, therefore the regression rate equation is different than that for SRMs:

$$r = aG^n x^m$$

Where r is the fuel regression rate in m/s, G is the total propellant mass flux in kg/m^2*s, x is the distance down the port in m, and a, n, and m are regression rate constants which are determined experimentally for individual propellants. This regression rate equation applies to a particular axial distance along the combustion port, therefore an average regression rate is usually calculated along the entire length of the HRE for comparison purposes. These regression rate equations apply to the system if the effects of radiation heat transfer are negligible and convective heat transfer dominates. If the instantaneous regression rate down the port is approximately constant, the average regression rate can be described with:

$$r_{avg} = aG_{avg}^n L_p^m$$

Where r_{avg} is the average fuel regression rate along the port in m/s, G_{avg} is the average total propellant flux rate along the port in kg/m^2*s, and L_p is the port length in m. There are many different equations and models for evaluating the burning rate for a particular fuel depending on which mass flow regime it exists in. The equation provided in this paper is used as a rough estimate of regression rate and is not the most accurate model for a system.

Like SRMs, the heat transfer rate into the solid fuel as well at the net heat generation from fuel combustion are major controlling factors of combustion. However, there are different regimes governed by the amount of mass flux out of the engine. For high mass flux, combustion is controlled by chemical kinetics. For medium mass flux, combustion is controlled by diffusion. For low mass flux, radiation heat transfer becomes more dominant as convective heat transfer starts to diminish. If the regression rate is very low, there is the potential issue that the fuel grain underneath the current burning surface begins to melt or cook because of its long exposure in the thermal layer. This cooking of the fuel can result in engine chuffing, which is the melted fuel being removed from the engine and exposing a new layer of combustible fuel. The burning profile of the fuel in HREs are different than that of an SRM, the section of fuel that is closest in axial distance to the oxidizer injector usually burns at a faster rate than the fuel further down the chamber. For single cylindrical port HREs, this results in a truncated cylindrical burning surface that may present differences in thrust profile than a SRM equivalent configuration.

The oxidizers in HREs are typically in liquid state during storage and then are converted into their gaseous state upon entry into the combustion chamber. While a compressed gas oxidizer would work, storing the oxidizer as a liquid is much more efficient in terms of space and fuel density. This method of providing a more

Table 4. Common solid fuels used for HREs

Fuel	References	Characteristics
Plexiglass	[2, 20]	Readily available in tube shapes for simple combustion. Toxic combustion fumes.
Polyethylene	[2, 4, 8, 12, 15, 20, 32, 41]	Forms a very viscous melting layer which lowers the typical regression rate.
Polybutadienes	[1-6, 8, 9, 11, 12, 15-17, 19-22, 28, 38, 39, 42]	Very common fuel for HREs, used as a binder in SRMs.
Paraffin waxes	[1, 4, 5, 8, 15, 21, 32]	Poor structural integrity. Higher regression rate compared to HTPB. Generates a low viscosity, instable, melted wax layer when combusted. Low cost material. Non-toxic combustion products.
Polyethylene Waxes	[32]	Generates a low viscosity, instable melted layer like paraffin waxes. High regression rate. Higher melting point than paraffin wax.
Acrylonitrile Butadiene Styrene (ABS)	[4, 5, 42]	Low cost material. Can be used to additively manufacturer complex port geometries.

Table 5. Common liquid oxidizers used for solid-liquid HREs.

Oxidizer	References	Characteristics
Liquid Oxygen	[2-4, 6, 8, 20]	Very common oxidizer. Efficient form of oxidizer due to only being O_2, there are no other inert molecules that do not aid in combustion such as the nitrogen in nitrous oxide.
Hydrogen Peroxide	[2-4, 6, 20, 41]	Referred to as High-Test Peroxide. Used as oxidizer and monopropellant. The peroxide is injected across a catalyst bed that separates the molecules into steam and oxygen. This heat generative decomposition reaction may cause issues with heat sensitive parts prior to the combustion chamber.
Nitrogen Tetroxide	[6, 20]	Naturally has a relatively high freezing point. If the desired freezing point is lower, nitric oxide can be added to the compound.
Nitrous Oxide	[3-6, 15, 32, 42]	Common oxidizer and monopropellant with higher specific impulse than hydrogen peroxide. Typically decomposed using a catalyst.

Table 6. Common additives for accelerating regression rate of solid fuel in HREs.

Additives	References
Aluminum	[2, 4, 5, 8, 9, 11, 12, 15, 19, 20, 27, 32, 37, 39]
Magnesium	[8, 32]
Magnesium Hydride	[8]
Lithium	[2, 32]
Lithium Hydride	[35, 36]
Lithium Aluminum Hydride	[1, 2, 4]
Boron	[9, 32, 37]
Triaminoguanidinium Azotetrazolate	[32]
Ammonia Borane	[32]
Copper Chromite	[4, 28]
Coal	[39]

compact storage of the oxidizers has the most potential applications and is why most research on direct HREs pertains to those which utilize a liquid oxidizer and solid fuel.

Another method for increasing the regression rate of solid fuel in HREs is the grain configuration. Fuel Regression Rate in Hydroxyl-Terminated-Polybutadiene/Gaseous Oxygen Hybrid Rocket Motors [19] has experimentally seen a dependence on grain port diameter and regression rate. Through advancements in 3D printing technology, the solid propellant grain in HREs can be printed into geometries that were previously impossible with casting or extruding manufacturing, e.g. helix port configuration. These complex 3D structures cause increased friction on the surface of the grain, resulting in increased heat transfer to the fuel grain and consequently lowering the energy required for combustion.

Choice of Fuel and Oxidizer for HRE

There are various types of fuels used for HREs, most of the work being done utilizes hydroxyl-terminated polybutadiene (HTPB) or a type of wax. It should be noted that not all of these fuel and oxidizers may be compatible. *Approaches to Low Fuel Regression Rate in Hybrid Rocket Engines* [32] lists several common combinations of fuels and oxidizers. Table 4 and Table 5 list several commonly used fuels and common oxidizers, respectively.

Because of its energy density as well the ability to safely handle it, HTPB is a very popular fuel choice for hybrid engines. HTPB is also commonly used in SRMs as binder that also behaves as a fuel. The most common gaseous oxidizers, for those few rockets that use a compressed gas oxidizer reservoir, are gaseous oxygen (GOX) and nitrous oxide (NOX), however most rockets further compress or chill these gasses until they are in their liquid phase which allows for more oxidizer to be carried on the rocket. Liquid oxidizers are transformed into gaseous phase upon entry to the combustion chamber to react with solid fuel, hydrogen peroxide for example is injected across a heated catalyst bed of silver to be effectively and rapidly decomposed into hydrogen and oxygen gasses for combustion.

Additives for HRE Propellant

The list of additives in Table 6 used to modify the regression rate for HREs is scarce compared to that of SRMs due to the fact that molecules that could act as oxidizers are not desirable in most cases. Many additives for increasing the regression rate of the fuels in HREs are metals that have high heats of reaction and high thermal conductivity. High nitrogen ingredients such as triaminoguanidinium azotetrazolate (TAGzT) can also be used to increase the regression rate, even though they do not have any oxygen atoms, they still provide positive heats of reaction and react at a fast rate. High temperature nitrogen can also react with aluminum particles to form AlN which may be beneficial to conserve oxygen for combusting compounds that require it.

Much research being done on rockets, and hybrid rocket engines specifically, focuses on increased the regression rate of the fuel to provide higher thrust. Since HREs have characteristically low fuel regression rates, there has not been a lot of research into further lowering the regression rate using additives. If the desired regression rate is less than what is naturally achieved for a given fuel and oxidizer mixture, it is reasonable to assume several of the additives listed in Table 2 that do not behave as oxidizers could be used to further lower the regression rate.

In direct hybrid engines the oxidizer traditionally goes from a liquid state to a gaseous one, which would require any oxidizers to also change state at the same properties as the oxidizer, which is why most additives are added to the solid fuel to modify the regression rate. However, liquid oxygen has been doped with fluoride (FLOX), to create a high performing oxidizer, but it is also highly toxic, thus increasing safety concerns.

Rocketry Applied to Power Generation

Hybrid rocket engines have been the subject of much research over the past several decades with many fuels and oxidizers being tested. One common characteristic of the fuels evaluated in that research is low cost materials. Low cost materials such as ABS and polyethylene can be utilized in combustion chambers and mixed with simple oxidizers such as liquid or gaseous oxygen. Through several modifications and advancements, a traditional gas turbine engine combustor could be modified to handle solid propellant grains. This modification would provide an alternative energy source for power generation if the engine components downstream of the combustor can handle the increased temperature of and pressure from solid fuel combustion. If these engines components are equipped with high-temperature materials, the increased heat generation from burning solid fuels compared to that of gasoline could provide greater output to the shaft turbine.

Demand for Hybrid Energy Sources for UAVs

Hybrid electric propulsion systems with more than one energy sources for powering UAVs have been the focus of intensive research. The reason for this is the huge success of applying hybrid power to highway vehicles. It significantly improved pollution and energy efficiency. UAVs that require increased distance and long duration flights could benefit significantly from a method of charging the on-board batteries. Traditional methods of charging on-board batteries, such as solar panels, are very inefficient in the terms of power generation per unit of mass. The US Department of Defense has been the leading organization funding research and the application of hybrid engine to its UAVs. Because it provides military UAVs long flight duration, reduced exhaust, and better efficiency.

Other commercial organization prefers the hybrid to a single conventional internal combustion because the electric side of the hybrid gives the UAVs more thrust in demanding task such as climbing and maneuvering in disaster, hazard environments while the liquid fuel, solid fuel or fuel cell is used for longer flight time. The electric – batteries which are continually being charged as the UAVs undergo their mission serves as a backup energy source. A hybrid energy source could allow drones to be used at higher altitudes for longer, travel further distances, or pollute less.

Method for Staging Multiple Solid Propellants in a Combustor

A pulse rocket motor design allows the solid propellants to be burned in sections however contained in a single case. The objective is to control the burn rate by using multiple solid propellants attached to each other with a buffer, a thick thermal barrier membrane, in between the solid propellants. The initial propellant is ignited and completely burn while the barrier inhibits the next section to be burnt only until after its ignited thus allowing us to control the start of the burn hence timing. Once ignited, the burn from the next propellant section destroys the barrier membrane. This provides control since each section can use the same or different solid propellant material to control the thrust level, burn rate and specific impulse. How quickly the barrier membrane burns can also be controlled to achieve desired performances since it's protected from the high temperature burning heat by the first propellant. Chiyako Mihara and Katsunori Ieki in their patent US8397486B2 achieved this by creating a two-pulse rocket motor with multiple ignitors set at the end of the propellants. As mention in the article, "According to the two-pulse rocket motor of the second or third means, the barrier membrane is divided into two pieces and a joint part is provided to weaken a portion to be broken or a slit is formed in the barrier membrane to break the barrier membrane. Therefore, the barrier membrane is surely broken at an expected position (weak part) by the pressure of gas generated by the operation of the second igniter or second propellant combustion."

Conclusion

From the research evaluated in this paper, multiple elements must be considered upon choosing a solid fuel for an application. Utilizing a SRM comes with multiple tradeoffs compared to using an HRE. SRMs have reduced complexity, increased thrust output, and the regression rate can be easily modeled. However, these motors cannot be easily shut off, there is no way to throttle the thrust output, and the premixed oxidizer and fuel have increased instability and safety is a concern. In contrast, HREs can be throttled and they have increased safety from separating the fuel and oxidizer. The tradeoff of using HREs are the lower regression rate, complex burning characteristics, and increased design complexity by adding an oxidizer tank, routing pipes, and injectors. Each of these elements should be considered when choosing a rocket for a particular application. After the decision to either mix the oxidizer with the fuel or keep them separated has been resolved, methods for altering the regression rate for both SRMs and HREs stem from the fuel and oxidizer choice and the addition additives. The choice of fuel and oxidizer seems to have the greatest influence on fuel regression rate and should be used to get the system in a close range to the target regression rate. To precisely tailor the regression rate, additives can be chosen for the appropriate propellent (either oxidizer mixed or separate) and varied in concentration to achieve the desired effect.

With the extensive research done into low cost fuels and the naturally low regression rate of hybrid rocket engines, HREs seem to be a likely candidate for power generation. Specifically, these HREs could be utilized aboard long distance/duration UAVs to provide power and charge on-board batteries. The UAVs primary propulsion method would still primarily be electric batteries for the ideal maneuverability, with power generation stemming from a turbine downstream of the HRE combustor. The hybrid rocket engine adds many benefits to the system compared to that of traditional gasoline engines charging on-board batteries. One of the greatest being the ability to operate at high altitudes due to the oxidizer being carried on-board the UAV. This type of innovation would also put safety at the forefront with propellants that have low sensitivity to impact and can be transported easily and less costly.

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