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# Hybrid Rocket Studies Using HTPB/Paraffin Fuel Blends in Gaseous Oxygen Flow

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## Abstract

Hybrid rockets have superior safety, versatility, and reliability over solid or liquid propellant rockets. However, low solid fuel regression rates and corresponding low thrust have hindered their application and utilization. Paraffin fuels regress significantly faster than traditional polymeric fuels, such as HTPB, and paraffin inclusion in HTPB represents a potential tool for performance augmentation in hybrid rockets. A comprehensive literature survey regarding mixed HTPB/paraffin fuels for hybrid rocket applications is presented herein. Plain HTPB; plain paraffin; and HTPB loaded with 10, 25, 50, and 75% paraffin fuel specimens were manufactured by inclusion of molten paraffin at elevated temperatures. The prepared fuel grains were burned in gaseous oxygen on a lab-scale hybrid rocket at moderate oxidizer mass fluxes (7-130 kg/m$^2$·s) and low pressures (0.2-0.9 MPa). Plain paraffin fuel exhibited a 300% increase in regression rate over plain HTPB. However, none of the mixed fuel formulations exhibited notable regression rate enhancement at the evaluated operating conditions.

## 1. Introduction

Hybrid rocket engines have unique advantages in comparison to pure solid or liquid propellants, including inherent safety, grain robustness, propellant versatility, simple mechanical design, low temperature sensitivity, potential throttlability, and low relative cost. However, there also exist disadvantages including low volumetric loading, potential fuel residuals, mixture ratio shift during motor firing, and mixing and combustion inefficiencies. The most commonly cited drawback of their performance is characteristically low solid fuel regression rates. Research efforts devoted to overcoming this shortcoming have led to numerous fuel regression rate enhancement strategies including utilization of non-traditional fuels and oxidizers; manipulation of oxidizer flow to yield unique flows, such as swirl or vortex flows; inclusion of energetic additives such as metals, metal hydrides, and solid oxidizers; and augmentation of combustion port geometry to yield increased burn surface area.

In the 1990s, researchers at the U.S. Air Force Research Laboratory (AFRL) performed combustion experiments with solid cryogenic fuels in a hybrid rocket configuration.[1-3] Their motivation was the stabilization and combustion of high-energy density matter, but their experimental results showed significant increases in regression rate as well. Carrick and Larson [1] demonstrated regression rate increases of 5-10 times for solid ethylene and n-pentane burning in a gaseous oxygen (GOX) crossflow in comparison to PMMA. Larson et al. [2] and DeRose et al. [3] completed high-pressure (800 psia) and high oxidizer flux (600 kg/m$^2$·s) testing on ten cryogenic, solid hydrocarbon fuels and observed regression rates that were 2-8 times larger than traditional HTPB fuel. A modified regression theory to account for the significantly increased regression rates of these fuels was not proposed by the researchers. However, Larson et al. [2] suggested the high regression rates of cryogenic fuels could be attributed to larger blowing coefficients, since the required specific energy for fuel gasification is approximately 20 times smaller for cryogenic fuels in comparison to traditional polymeric fuels. Several researchers at Orbital Technologies Corporation later completed combustion testing on several cryogenic hybrid systems and reported similar results.[4-6] Development testing included cryogenically frozen paraffin wax and kerosene.[5]

Following these studies, researchers at Stanford University began experimenting with long-chain, paraffin-based hydrocarbons with melting temperatures above room temperature.[7-9] Karabeyoglu et al. [7] analyzed the previously mentioned combustion tests completed at AFRL [1-3] and argued that the observed high regression rates of the cryogenic fuels could not be completely explained by their low heats of vaporization and altered blowing parameters. Furthermore, Karabeyoglu et al. [7-8] postulated a mass transfer mechanism, in addition to fuel

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vaporization, in which a melt layer exists on the fuel surface. The experimental program successfully demonstrated that the high-speed oxidizer flow across this melt layer leads to liquid instabilities and subsequent droplet formation and entrainment into the oxidizer flow stream. The regression rate of fuels exhibiting the entrainment mass transfer mechanism is enhanced due to: 1) a reduction in enthalpy difference between the flame and surface because the surface fuel is in the liquid phase; 2) a reduction in the effective heat of gasification because the entrained fuel droplets only require a heat of fusion which is generally significantly less than the heat of vaporization; 3) an increase in convective heat transfer due to a reduction in the blocking effect from gas injection at the fuel surface; and, 4) an increase in convective heat transfer stemming from an increased surface roughness associated with the liquid layer instabilities.

Karabeyoglu et al. [7-8] developed a melt layer hybrid combustion theory to predict regression rates in fuels that exhibit fuel entrainment and were able to successfully predict the regression rates of the cryogenic hybrid fuels evaluated at AFRL [1-3] and paraffin wax. Karabeyoglu et al. [9] later refined the theory to include supercritical operation and predict the regression rates of the entire series of homologous normal alkanes ($C_nH_{2n+2}$) with a reasonable degree of success. The expanded theory indicated that paraffin waxes are the best candidates for solid fuels in hybrid rocket engines among the series of *n*-alkanes. Stanford researchers also developed a specific paraffin-based fuel formulation (SP1a) and have evaluated its combustion performance at several facilities under numerous oxidizer flows (GOX, LOX, $N_2O$), a wide range of oxidizer fluxes (10-400 $kg/m^2 \cdot s$), and at large scales of up to 6 000 $lb_f$ of thrust. [7, 10]

Weinstein and Gany [11-13] further expanded the regression rate theory to include liquid flow along the fuel surface into the combustion chamber, which becomes relevant at lower oxidizer mass fluxes. It was suggested that this fuel loss mechanism should be considered because it potentially has significant consequences on the combustion efficiency of the hybrid rocket.

Karabeyoglu and Akron [14] claim the benefits of paraffin fuels, in comparison to traditional polymeric fuels, include: 1) low cost and high availability; 2) high performance including specific impulse, regression rate, and fuel utilization; 3) non-toxicity; 4) virtually infinite shelf life; and 5) hydrophobic nature which allows for sensitive, high-energy additive incorporation. The commonly cited drawbacks of utilizing paraffin-based fuel include 1) potentially lower combustion efficiencies due from ejection of entrained but unburned fuel droplets, and 2) poor mechanical properties that make scale-up difficult. Numerous mechanical property enhancement strategies have been employed, and one common method is the inclusion of polymer additives [15-16]. However, even the structurally enhanced SP1a fuel developed at Stanford displayed mechanical failure in several scale-up tests.[10]

Mixed fuel systems, consisting of two or more fuel components, represent a potential strategy to yield improved hybrid rocket performance. Hybrid rockets combine solid and liquid propellants to yield distinct advantages that were not present in either constituent. Similarly, the combination of HTPB and paraffin in a heterogeneous fuel system could yield attributes of each constituent, such as the good mechanical properties of HTPB and the high regression rates of paraffin. Furthermore, mixed binder systems potentially represent unique tools for tailoring the performance of hybrid rocket propulsion systems to a particular design through variation of the fuel composition. However, variation of the fuel composition in a paraffin/HTPB mixed fuel system does not significantly affect the delivered specific impulse ($I_{sp}$), as shown in Figure 1.

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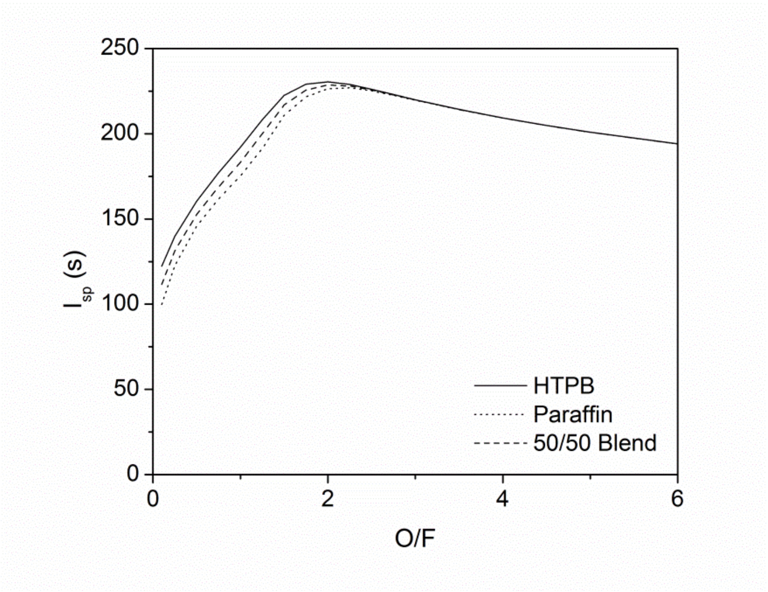

Figure 1: Theoretical performance of plain HTPB, plain paraffin, and a 50/50 fuel blend burning in GOX at a chamber pressure of 1 000 psia (6.9 MPa) with equilibrium composition, as evaluated by NASA's CEA.

The following section provides a comprehensive literature review on the subject of mixed HTPB/paraffin fuel systems for hybrid rocket applications. An experimental methodology section provides a brief summary of the testing apparatus and applied methodologies. The results and discussion section presents the measured regression rates of fuel specimen comprised of plain HTPB, plain paraffin, and HTPB loaded with 10-75% paraffin burning in gaseous oxygen, and compares these results to literature findings. A conclusion section summarizes the observed experimental trends and highlights key points.

## 2. Literature Review

Many research efforts have focused on the evaluation of HTPB/paraffin fuel blends for hybrid rocket applications, mainly through thermal degradation [17-19, 23, 25] and combustion [11, 17, 26-27, 29-32, 34] experiments. This section of the paper serves to provide a thorough and comprehensive review of all contributions thus far to the topic.

### 2.1 Thermal Degradation Studies

Sakote et al. [17] investigated TDI-cured HTPB fuel containing 35%, 50%, and 65% paraffin concentrations by mass. Fuel samples were manufactured by mixing of heated HTPB with molten paraffin, and allowing the mixture to cure at 65 °C for 3-5 days. Simultaneous TGA and DTA experiments were performed in a nitrogen atmosphere from 10-500 °C at a heating rate of 10 K/min. All samples exhibited two major stages of mass loss which onset near 200 °C and 425 °C. The first stage of mass loss was more significant, and increased from 56% to 72% with an increased paraffin loading of 35% to 65%. DTA thermograms for all fuel samples displayed similar behavior, and exhibited an endothermic peak near 60 °C, an exothermic peak near 200 °C, an endothermic peak near 325 °C, and a set of two exothermic peaks near 425 °C. The first endothermic peak near 60 °C is due to paraffin melting. The set of exothermic peaks near 425 °C differed between compositions due to differing concentrations of bounded and unbounded paraffin, as confirmed by SEM analysis. Sakote et al. [17] suggested that this set of exothermic peaks, and the differences between each composition at this decomposition stage, indicates that the HTPB and paraffin are bounded at the molecular scale and that each constituent melts at different temperatures.

Sinha et al. [18] reported on the thermal decomposition of TDI-cured HTPB fuel containing 0-27.75% paraffin as determined through TGA and DSC experiments at heating rates of 3-43 K/min from 30-520 °C in a Helium atmosphere. Mixed fuel samples were prepared by mixing a slurry of liquid pre-polymer, paraffin, and curative at elevated temperature with subsequent curing at elevated temperature for 5 days and room temperature for 5 days. The pure HTPB fuel samples exhibited two mass loss stages in the TGA and DSC curves, and representative results from the heating rate of 3 K/min are reported, as follows. The first mass loss was comparatively small, occurred near

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300 °C, and can be attributed to breaking of the urethane linkages formed during the polymer curing process and subsequent evaporation and decomposition of the curative material. The second mass loss stage occurs near 425 °C and can be attributed to depolymerization and decomposition of the remaining HTPB fuel. In general, increasing the heating rate slightly increased the first stage mass loss; shifted the decomposition onset temperatures of both stages to higher temperatures; and deceased the net exothermicity and endothermicity of the first and second stages, respectively. Mixed fuel samples, with paraffin fuel included, exhibited similar behavior to pure HTPB samples. The inclusion of paraffin in the fuel system did not significantly affect the last mass loss stage. However, an additional endothermic stage with no corresponding mass loss was present near the paraffin melting temperature of approximately 50 °C. Additionally, the mass loss associated with the next stage significantly increased with an accompanying decrease in exothermicity, without a significant change in the decomposition onset temperature. These trends were more prevalent with higher paraffin loading, and the first stage mass loss was doubled for the highest paraffin loading of 27.75%. Furthermore, these trends were attributed to the volatilization of paraffin between 300 and 320 °C.

Sinha et al. [19] also measured the heats of combustion of the mixed fuel systems and reported small increases associated with paraffin inclusion, as expected. Mechanical properties of the fuel specimen were evaluated through DMA experiments and showed significant alterations in stiffness and storage modulus with even the lowest paraffin loading.

Sinha et al. [18] further utilized the collected DSC data to determine thermal degradation kinetic parameters of all evaluated fuel mixtures. The inclusion of paraffin led to a reduction in the activation energy, reaction rate constant, and frequency factor for the first decomposition stage, and these trends were more prevalent with additional paraffin loading. The activation energy and reaction rate were also decreased by the inclusion of paraffin for the second decomposition stage, but the frequency factor was not significantly affected, and additional paraffin loading did not further alter the kinetic parameters. Sinha et al. [19] also measured the temperature-dependent specific heat capacity of these fuel blends during DSC experiments. Paraffin inclusion led to a significant reduction in the fuel blend's specific heat capacity, and the highest paraffin loading of 27.75% led to a 50% decrease from approximately 1.6 to 0.8 J/g·K at 80 °C. The collected kinetic parameters and specific heat capacity data were coupled and utilized to calculate the pyrolysis rates of fuel samples, according to methods reported by Lengelle et al. [20-22]. These calculations indicated paraffin inclusion in the mass range of 12.25-27.75% leads to an increase of 5-33% in fuel pyrolysis over pure HTPB fuel in an inert atmosphere. The reported increases are due to a reduction in activation energy and increase in fuel vaporization and should not be confused with the previously mentioned entrainment effect.

Cardoso et al. [23] performed TGA experiments with pure HTPB, pure paraffin, and a mixed fuel system at heating rates of 5-15 K/min under a 100 mL/min oxidant flow. The mixed fuel system was prepared by addition of paraffin particles to an HTPB slurry and subsequent curing with IPDI. The pure HTPB samples showed two stages of major mass loss onset at approximately 300 and 425 °C. The first stage can be attributed to breaking of the urethane bonds formed during the curing process, and the second stage can be attributed to depolymerization, cyclization, and crosslinking processes. The pure paraffin sample showed two stages of mass loss onset at approximately 200 and 425 °C, due to elimination of volatile compounds, water, and low molecular weight hydrocarbons, and due to decomposition of higher molecular weight compounds, respectively. The mixed fuel system, which contained 60% mass loading of paraffin particles, also showed two major mass loss stages. The onset temperature of the first stage was slightly shifted to a lower temperature of approximately 200 °C, and the corresponding mass loss significantly increased from roughly 10% to 35%.

Cardoso et al. [23] also utilized the TGA mass loss data to calculate the activation energy of the fuel samples according to the Ozawa-Wall-Flynn method [24]. The pure HTPB and paraffin samples exhibited single activation energies over the measured temperature range of approximately 300 and 100 kJ/mol, respectively. However, the mixed fuel system exhibited an activation energy of 150 kJ/mol at lower temperatures and 300 kJ/mol at higher temperatures. These findings suggest the decomposition of the fuel mixture requires a two-step kinetics model rather than a single-step model that applies for the pure fuel systems. This finding is significant because one of the assumptions made in the evaluation of pyrolysis rates from thermal degradation kinetics is that the degradation reaction is first order [24]. Accordingly, pyrolysis rates of mixed HTPB and paraffin fuel systems may be inaccurate when determined according to these methods.

Hu et al. [25] evaluated HTPB/paraffin fuel blends containing aluminum, magnesium, ammonium perchlorate, and carbon black additives through DSC and TGA experiments at a heating rate of 20 K/min under air and nitrogen gas flows (30 mL/min) at temperatures from 20-750 °C. No information was provided regarding fuel sample preparation

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and manufacturing procedures. Mixtures without energetic additives were not presented, with the exception of a plain HTPB sample, so direct comparison to other experiments cannot be made. However, a reduction in the HTPB loading and corresponding equivalent increase in the paraffin loading in additive fuel samples led to increased mass loss at the first stage of decomposition, which is in agreement with the previously reported results.

In general, the findings of Cardoso et al. [23] are in good agreement with the experiments completed by Sinha et al. [18-19]. However, Sinha et al. [18] noted a 35% mass loss in the first decomposition stage with the addition of only 27.75% paraffin, while Cardoso [23] noted a 35% mass loss corresponding to a 60% paraffin loading. The two notable differences between the experiments were that Sinha et al. [18] utilized an inert Helium atmosphere and included paraffin as a dissolved liquid during the fuel mixing process, while Cardoso et al. [23] utilized an oxidant atmosphere and included paraffin as dispersed solid particles during the mixing process. The differences is their results highlight the importance of how atmospheric composition and paraffin inclusion procedures can play a significant role in mixed fuel system decomposition under heating in quiescent conditions.

## 2.2 Hybrid Rocket Studies

Lee and Tsia [26-27] evaluated the combustion of IPDI-cured HTPB loaded with 50%, 70%, and 90% paraffin in GOX and nitrous oxide core flows with axial and swirling flow configurations on a lab-scale hybrid motor. Oxidizer mass fluxes and chamber pressures were tailored through means of a pressure regulator and interchangeable nozzles and were varied in the ranges of 1.4-3.5 MPa and 50-500 kg/m$^2$·s, respectively. Mixed fuel samples were prepared by mixing molten paraffin and heated HTPB at a temperature of 80 °C, and curing procedures were carried out according to general HTPB curing practices. In addition to spatially and temporally averaged regression rate data, transient regression rate data was deduced from the burn reconstruction method developed by George et al. [28]. The researchers stated the mixed fuel grains loaded with 70% and 90% paraffin were not structurally sound and resulted in ejection of significant unburned fuel through the nozzle and unstable combustion at higher oxygen mass fluxes.[26] The addition of 50% and 90% paraffin to plain HTPB led to approximate regression rate increases of 10% and 150%, respectively, under non-swirling GOX flow at an oxidizer mass flux of 250 kg/m$^2$·s. This finding suggests that a minimal paraffin loading may be required prior to realization of any useful regression rate enhancement.

Boronowsky [29] evaluated the combustion of plain HTPB, plain paraffin, and HTPB loaded with 15% and 30% paraffin spheres (0.3-0.7 mm) in low GOX flow (15-60 kg/m$^2$·s) and low pressures (< 0.7 MPa) on a lab-scale hybrid motor. Boronowsky's intentions for including spherical paraffin in a non-homogenous fuel mixture, instead of liquid paraffin in a homogenous mixture, were to 1) not further complicate the curing process of HTPB fuel, and 2) yield the regression rate benefits of paraffin without compromising the structural integrity of the fuel grain. Utilization of spherical paraffin may also lead to a rougher fuel surface during combustion, once the paraffin spheres are removed from the fuel surface or become entrained into the core flow, and could lead to enhancement of turbulence and heat transfer. Boronowsky made notes on potential modeling complications but did not make a significant effort to model the regression of the mixed fuel system. In particular, an accurate regression rate model would need to account for alterations in the gas properties due to variations in fuel chemistry, adjustments of the skin friction coefficient due to additional roughness, and modifications to the blocking factor. [29] It is worth noting that after combustion testing was completed on all fuel formulations, regression rate prediction of mixed fuel compositions was completed through volumetric weighting of the empirical regression rate expressions of the base fuel formulations with some success.

The fuel formulation containing 30% paraffin spheres showed signs of mechanical weakness due to a lack of bonding between the paraffin and HTPB. The addition of 15% and 30% paraffin spheres to HTPB led to 25% and 40% increases in regression rate, respectively, at the higher evaluated oxidizer fluxes.[29] The measured regression rates for baseline HTPB and paraffin do not agree with literature values and are significantly larger than reported elsewhere. A number of factors could cause this discrepancy including the small motor scale (5x2 cm), but the probable culprit is the average oxidizer mass flux calculation methodology which is not presented within the paper. The reported oxidizer mass flux appears to be calculated through an average of the initial and final oxidizer mass fluxes, which can yield significant error for even small changes in the combustion port diameter [25]. Regardless, the presented results can still be considered on a relative scale to each other, and serve as a proof-of-concept for the proposed enhancement technique.

Boronowsky [29] noted that the 30% paraffin-loaded fuel samples generated an audible noise during combustion testing, but no discrepancies were present in pressure or thrust data traces. Furthermore, Boronowsky suggested this

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sound may be related due to ejection of unburned paraffin pieces. There likely exists a confounding limit of paraffin sphere size and concentration for stable and efficient combustion, that is also dependent on hybrid motor scale.

Boronowsky [29] also made several homogenous mixed fuel samples by including liquid paraffin during the curing process. The paraffin concentration was not specified, but was likely similar to other fuel samples and on the order of 15-30%. Although the mixed fuel samples exhibited good mechanical properties, combustion testing did not show any significant regression rate enhancement. This result is in agreement with the findings of Lee and Tsia [26], and may support the hypothesis that a minimal paraffin loading may be required prior to realization of any useful regression rate enhancement. It is also worth noting that this experimental observation is in conflict with the thermal degradation studies of Sinha et al. [18-19] and Cardoso [23], in which inclusion of paraffin as a molten liquid led to more significant pyrolysis enhancement than inclusion of paraffin spheres. The combination of these experimental observations may further suggest that the surface roughness increase produced by removal of paraffin spheres at the fuel surface is indeed significantly enhancing turbulence and heat transfer processes.

Weinstein and Gany [11] and Sisi and Gany [30] burned pure paraffin, pure PMMA, and HTPB/paraffin (1:1) mixed fuel in a nitrous oxide core flow at low oxidizer mass fluxes (20-50 $kg/m^2{\cdot}s$). Additionally, the mechanical properties of the fuels were evaluated through uniaxial compressive testing at a displacement rate of 5 mm/min. The mixed fuel specimens were manufactured by mixing paraffin particles (0.5 mm) into pre-polymerized HTPB and allowing for binder curing at room temperature. Mechanical property testing demonstrated that the mixed fuel system had significantly more elasticity than the pure paraffin fuel. The combustion data were analyzed to yield average regression rates and combustion efficiencies. The regression rate of the mixed fuel fell in between that of the pure fuels and exhibited an oxidizer mass flux exponent that was reduced from 0.67 for pure paraffin to 0.59 for the mixed fuel system. Combustion efficiencies on the order of 80-100% were achieved and were generally higher for the mixed fuel system in comparison to the pure paraffin fuel. Combustion tests with the pure paraffin fuel exhibited residual fuel mass in the post-combustion chamber and larger exhaust plumes stemming from unburned fuel ejection, but these phenomena were not present in the mixed fuel system. This burning behavior alteration was attributed to the variation of the fuel systems' mechanical properties [30], but may actually be linked to the lack of a melt layer on the fuel surface.

A group of students at the University of Washington [31-32] designed and built a sounding rocket based on a HTPB/paraffin fuel system burning in a nitrous oxide core flow. The team's fuel was based on paraffin for high regression rates, and 10% HTPB was added as a structural agent. Unfortunately, useful diagnostics were not presented, so no comparison can be made between the motor firing data and other literature.

Research efforts at the SPLab at Politecino di Milano have also focused on the inclusion of paraffin in HTPB fuel systems. DeLuca et al. [33] applied statistical-thermodynamic modeling and estimated a homogenous paraffin saturation limit between 60 and 70%. Subsequent curing tests showed a loss of mixture stability between 60 and 70% loading, as evidenced by mass loss after mixture curing. Uni-axial tensile testing at a displacement rate of 50 mm/in showed a significant increase in elasticity accompanied by a small reduction in strength due to the addition of 50% paraffin to the plain HTPB fuel. Ignition and combustion evaluations have also been completed, but not yet reported, and indicated no measureable regression rate enhancement with the inclusion of molten paraffin in an HTPB fuel matrix.(Personal Communication, May 19, 2017)

In addition to the previously detailed thermal degradation studies, Sakote et al. [17] also evaluated HTPB fuel loaded with 35%, 50%, and 65% paraffin burning in a swirling GOX core flow at moderate oxidizer mass fluxes (70-90 $kg/m^2{\cdot}s$). As previously mentioned, fuel samples were prepared by mixing heated HTPB and molten paraffin and allowing the mixture to cure at 65 °C for 3-5 days. One fuel sample of each formulation was burned at the same initial conditions for a total time of 5 s, and the post-combustion fuel grains were cut and measured with calipers to determine the spatial fuel regression. No baseline HTPB or paraffin motors were burned, so a direct comparison cannot be made. However, average regression rate increases of 10% and 12% were noted when increasing the paraffin content from 35% to 50% and from 50% to 65%, respectively.[17]

From the present authors' group, Thomas et al. [34] evaluated the performance of a HTPB/paraffin fuel blend loaded with 10% paraffin burning in gaseous oxygen (10-150 $kg/m^2{\cdot}s$) at moderate pressures (< 1.5 MPa). [34] The mixed fuel system was prepared by inclusion of molten paraffin at elevated temperature and led to a 20% increase in regression rate across the tested oxidizer mass flux range.

There is no general consensus on the effects of paraffin inclusion in HTPB on combustion behavior and regression rate enhancement. Combustion studies presented by Lee and Tsai [26-27] indicate that when paraffin is included as a

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molten liquid, a high loading is necessary for notable regression rate enhancement, which is in agreement with the findings presented by Boronkowsky [29]. Boronkowsky [29] directly compared the combustion of fuel blends containing paraffin included as a molten liquid and as spherical particles, and found that spherical particle inclusion is the only method that leads to regression rate enhancement at low mass loadings (< 30%). Combustion results presented by Sakote et al. [17] and Thomas et al. [34] are in direct conflict with these findings, and suggest useful regression rate enhancement can occur at lower mass loading, even when included as a molten liquid. The reasons for these discrepancies are not clear, but they could potentially stem from variation in motor scale or operating conditions.

### 2.3 Literature Summary

The preceding section served to review and compare all relevant literature pertaining to HTPB/paraffin fuel blends for hybrid rocket applications. Significant work has been completed towards the evaluation of the thermal degradation of these fuel blends. In general, inclusion of paraffin in an HTPB fuel leads to increased mass loss during the early stages of decomposition, which is more prevalent with further paraffin loading. Several research teams have evaluated the combustion of HTPB/paraffin fuel blends on lab-scale hybrid rockets and under various operating parameters. While some researchers report significant enhancement, others have reported little to no enhancement associated with paraffin inclusion. Discrepancies between both thermal degradation and hybrid rocket combustion studies indicate that a paraffin inclusion limit for noticeable enhancement may exist, highlight the importance of paraffin inclusion methodology (molten liquid versus solid particle), and suggest potential dependencies on operating conditions.

## 3. Experimental Methodology

The objective of the present project was to evaluate the regression rate enhancement and combustion behavior associated with the inclusion of paraffin in HTPB fuel burning in gaseous oxygen. Plain HTPB, plain paraffin, and mixed fuel specimens loaded with 10, 25, 50, and 75% paraffin were manufactured and burned in gaseous oxygen flow. Fuel specimen preparation methodology is presented in detail, as the inclusion method seems to play a significant role in potential enhancement. Detailed experimental procedures have been previously presented [35-36] and are briefly described for completeness.

### 3.1 Fuel Specimen Preparation

HTPB-R45M pre-polymer, IPDI curative, and FR 3032 paraffin were obtained from Firefox Enterprises, Sigma Aldrich, and CandleWic, respectively. All fuel samples were mixed by hand and cast into standard 1-in, schedule 40 PVC which serves as a motor casing. Plain HTPB fuel was prepared by mixing pre-polymer and curative at a cure ratio (-NCO/-OH) of one, followed by a vacuum cycle to remove entrained air bubbles. The resultant mixture was poured into the motor casing and allowed to cure for one week at a temperature of 63 °C. Plain paraffin fuel was prepared by heating the wax to 63 °C and casting the material into the motor casing by a modified spin-casting methodology. Mixed fuel samples were prepared by heating pre-mixed HTPB/IPDI and paraffin to 63 °C separately and then mixing the two constituents together at elevated temperature. The mixed fuel slurry was poured into a pre-heated motor casing and then allowed to cure for one week at 63 °C before cooling to ambient conditions. Cured fuel grains were cut to 5 cm in length, and a 2-mm combustion port was drilled through the center of each.

### 3.2 Combustion Testing

A simplified schematic of the experimental apparatus is shown in Figure 2. Pressure transducers, a K-type thermocouple, and the igniter are represented by P, T, and I indicators in Figure 2. The system is capable of operating in both constant oxidizer flow and blowdown tank configurations. In the constant oxidizer flow configuration, the pressure regulator is set to the desired level, and in the blowdown configuration, the blowdown tank is pressurized to the desired level.

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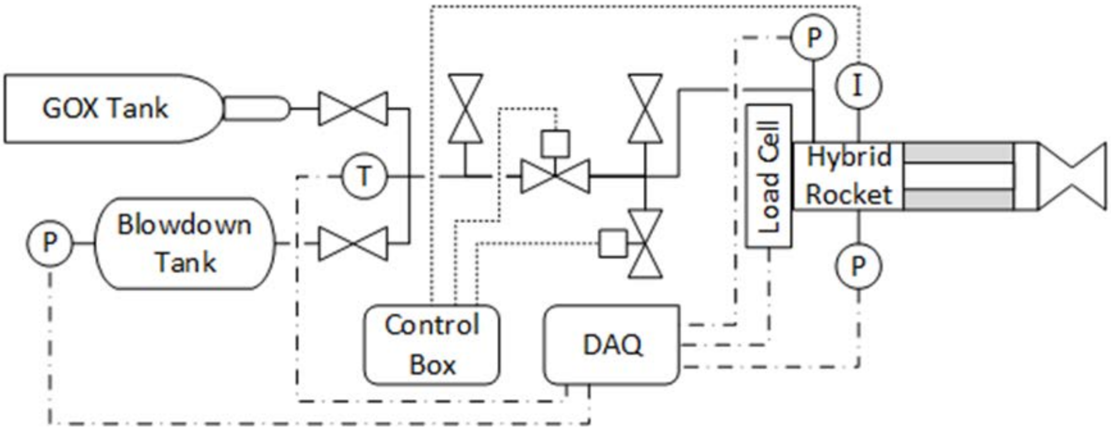

Figure 2: Schematic representation of the lab-scale hybrid rocket including oxygen and blow down tanks, plumbing system, telemetry (pressure transducers and thermocouple) locations, load cell, and hybrid rocket.

Pressure transducers just upstream of the injector and in the combustion chamber, coupled with a calibrated injector orifice, allow for transient measurement of the oxidizer mass flowrate. The mass of each fuel grain and the spatially dependent combustion port diameter were measured before and after each motor firing. Although the final combustion port diameter was directly measured in several locations, the regression rate was determined by the mass-loss method, described as follows. The post-burn combustion port diameter was calculated by:

$$D_f = \left[\frac{4(m_i - m_f)}{\pi \rho_f L} + D_i^2\right]^{1/2} \tag{1}$$

where $D_i$ and $D_f$ are the initial and final combustion port diameters, respectively; $m_i$ and $m_f$ are the initial and final fuel grain masses, respectively; $\rho_f$ is the fuel density; and $L$ is the fuel grain length. The average fuel regression rate ($\bar{\dot{r}}$) and oxidizer mass flux ($\bar{G}_{ox}$) are given, respectively, by:

$$\bar{\dot{r}} = \frac{D_f - D_i}{2t_b} \tag{2}$$

$$\bar{G}_{ox} = \frac{16\bar{\dot{m}}_{ox}}{\pi(D_i + D_f)^2} \tag{3}$$

where $t_b$ is the burn time, and $\bar{\dot{m}}_{ox}$ is the average oxidizer mass flow rate. Karabeyoglu et al. [37] evaluated numerous space-time averaging techniques and determined that diameter averaging, as shown in Equation (3), yields the lowest error for average oxidizer mass flux calculations. In addition to these calculations, the collected data were utilized to calculate average fuel mass loss, O/F ratio, chamber pressure, thrust, characteristic velocity, and specific impulse. Furthermore, several burn reconstruction techniques were used to deduce transient fuel mass flow, regression rates, and combustion efficiencies, but they are not described herein.

## 4. Results and Discussion

The measured fuel densities for all fuel grains are shown in Figure 3. The plain HTPB fuel specimen exhibited an average, measured density of 914 kg/m$^3$, which is comparable to the theoretical value of 930 kg/m$^3$. The as-received paraffin had density of approximately 865 kg/m$^3$, and the plain paraffin fuel specimen exhibited an average measured density of 853 kg/m$^3$. Marano and Holder [38-40] developed asymptotic behavior correlations (ABCs) to predict the thermophysical properties of n-paraffins. The paraffin wax utilized to make the fuel specimens herein has a manufacturer specification for melting temperature of 327 K. Employment of Marano and Holder’s ABC for the melting temperature of n-paraffins indicates the acquired paraffin wax has, on average, a carbon number of 25 (n-Pentacosane), which has a density of approximately 812 kg/m$^3$ [41]. The higher observed density of the paraffin indicates the presence of higher carbon number paraffins which have a higher melting temperature, viscosity, surface tension, thermal conductivity, and heat capacity. With the exception of the fuel samples loaded with 75% paraffin, the measured fuel densities closely follow the expected theoretical trend, depicted as a dashed line in Figure 3. The error bars in Figure 3 represent the standard deviation of the measured fuel density and may indicate the presence of some degree of fuel non-uniformity.

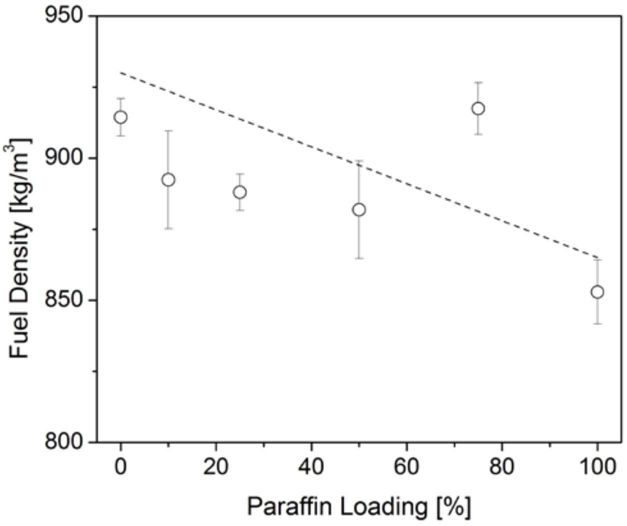

Figure 3: Fuel density measurements for plain HTPB, plain paraffin, and mixed fuel samples. The dashed black line represents the theoretical density of the fuel sample.

## 4.1 Combustion Tests

Testing conditions spanned a moderate range of oxidizer mass fluxes (7-130 kg/m$^2$·s) and low pressures (0.2-0.9 MPa). The average regression rate of all fuel grains burned in gaseous oxygen are plotted against the corresponding average oxidizer mass flux in Figure 4. The error bars in Figure 4 represent measurement error as determined by a root-sum-square error analysis. The solid and dashed lines represent least-squares regression fits of the data to a power law approximation for plain HTPB and plain paraffin, respectively. The empirical correlation for the plain HTPB data is given by:

$$r = 0.51 G_{ox}^{0.64} \tag{4}$$

where the units for regression rate and oxidizer mass flux are mm/s and kg/m$^2$·s, respectively.

The paraffin fuel grains exhibited a regression rate increase of approximately 300% over the evaluated testing conditions. In general, the mixed fuel systems performed similar to the plain HTPB fuels and did not exhibit measureable enhancements in regression rates at any paraffin loading between 10 and 75%. Although all data points lie within the experimental scatter, at higher oxidizer mass fluxes (> 90 kg/m$^2$·s), the mixed fuel systems appear to begin to outperform the plain HTPB fuel specimen. The observed lack of regression rate enhancement, even up to a paraffin loading of 75%, supports the hypothesis of a practical loading limit required prior to the realization of enhancement, but this explanation does not fully explain the observed results. These findings agree with the findings presented by Boronowsky [29], partially agree with the findings presented by Lee and Tsia [26-27], and are in conflict with the findings presented by Sakote et al. [17] and Thomas et al. [34]. One explanation for the observed trends is that the paraffin and HTPB are homogenously mixed, and the pyrolysis of HTPB dominates the regression process, so that no significant melt layer is formed during motor combustion. However, this explanation cannot fully account for the discrepancies between the current results and certain literature results.

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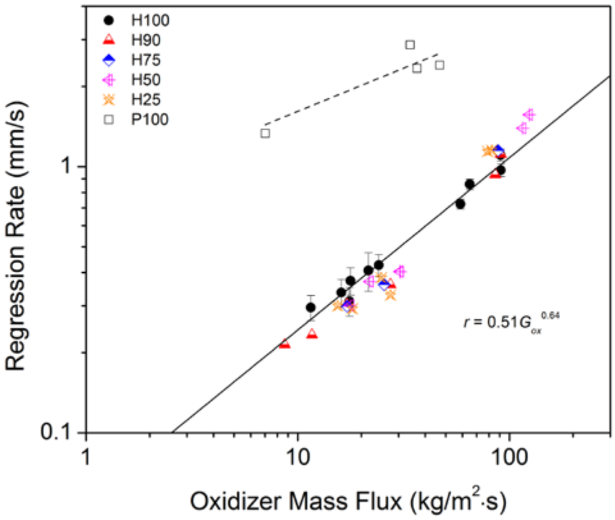

Figure 4: Measured regression rates for plain HTPB, plain paraffin, and mixed fuel systems burning in gaseous oxygen.

A summary of regression rate measurements of HTPB/paraffin fuel systems presented in the literature is shown in Table 1. Table 1 only includes studies where a direct comparison was made to a plain HTPB fuel specimen, so that the regression rate enhancement over the plain HTPB baseline could be evaluated. Furthermore, the hybrid rocket studies shown in Table 1 only include experiments with axially flowing gaseous oxygen. The data in Table 1 from the experiment performed by Boronowsky [29] include fuel mixtures with paraffin included both as a molten liquid and as a solid particle; however, the subsequent discussion will focus entirely on fuel mixtures where the paraffin as incorporated as a molten liquid.

There is some disagreement between the studies, but there are also clear trends. The four presented hybrid rocket studies support the argument for a practical paraffin loading limit for realizable regression rate enhancement, because all loadings below 90% exhibit little to no enhancement, specifically for when the paraffin is included as molten liquid. One explanation for the discrepancies between the presented results of the selected experimental studies is that the operating conditions may play a significant role in regression rate enhancement of the mixed fuel system. Within the dataset of the current study, the mixed fuel systems’ appear to begin to outperform the plain HTPB baseline at higher oxidizer mass fluxes (> 90 kg/m$^2$·s). The experiments of Boronowsky [29] showed no regression rate enhancement, and were conducted at low oxidizer mass fluxes (15-60 kg/m$^2$·s) and similar pressures. Lee and Tsai [26-27] observed a 10% regression rate enhancement for a paraffin loading of 50%, but their experiments were conducted at significantly larger oxidizer mass fluxes (50-500 kg/m$^2$·s) and chamber pressures that were approximately 300% larger than the current study and that of Boronowsky [29]. Thomas et al. [34] observed a 20% increase in regression rate for a paraffin loading of 10%, but their experiments were conducted at chamber pressures that were also approximately 300% larger than the current study and that of Boronowsky et al. [29]. This comparison of experimental results suggests the operating conditions of motor firings, specifically the oxidizer mass flux and chamber pressure, may play a role in the effectiveness of mixed fuel systems leading to regression rate enhancement. However, a comprehensive series of tests independently spanning a larger range of oxidizer mass fluxes and chamber pressures would be necessary to support this argument.

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Table 1: Summary of relevant regression rate results for HTPB/paraffin binders.

| Reference | Experiment | Paraffin Type/Loading | Enhancement |
|---|---|---|---|
| Sinha et al., 2015 | DSC<br>3-43 K/min, 30-520 °C | Molten Liquid, 12.25% | 5% |
| | | Molten Liquid, 27.75% | 33% |
| Lee and Tsia, 2008 | Rocket (180x41 mm)<br>50-500 kg/m$^2$·s, 1.4-3.5 MPa | Molten Liquid, 50% | 10% |
| | | Molten Liquid, 90% | 150% |
| Boronowsky, 2011 | Rocket (40x20 mm)<br>15-60 kg/m$^2$·s, < 0.7 MPa | Molten Liquid, 15-30% | - |
| | | Soid Particles (0.3-0.7 mm), 15% | 25% |
| | | Soid Particles (0.3-0.7 mm), 30% | 40% |
| Thomas et al., 2017 | Rocket (150x25 mm)<br>10-150 kg/m$^2$·s, < 1.5 MPa | Molten Liquid, 10% | 20% |
| Current Study | Rocket (50x30 mm)<br>10-130 kg/m$^2$·s, < 0.9 MPa | Molten Liquid, 10-75% | - |

## 4. Conclusion

The inclusion of paraffin in HTPB burning in gaseous oxygen as a regression rate enhancement strategy for hybrid rocket motors was evaluated by inclusion of molten paraffin at mass loadings ranging from 10-75%. The plain paraffin fuel exhibited a 300% increase in regression rate in comparison to plain HTPB, but none of the mixed fuel systems showed signs of regression rate enhancement at the tested operating conditions. These findings support some literature findings but are in conflict with other literature. It is evident from the current experimental results and the presented literature survey that the manufacturing procedures of mixed HTPB/paraffin fuel systems and the operating conditions, such as the pressure and oxidizer mass flux, could play significant roles in any potential regression rate enhancement. Further testing is necessary to fully characterize these blended fuel systems.

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