Formulation, Casting, and Evaluation of Paraffin-Based Solid Fuels Containing Energetic and Novel Additives for Hybrid Rockets

Daniel B. Larson,¹ John D. Desain,² Eric Boyer,¹ Trevor Wachs,¹ Kenneth K. Kuo,¹ Russell Borduin,³ Joseph H. Koo,³ Brian B. Brady,² Thomas J. Curtiss,² and George Story⁴

¹The Pennsylvania State University, University Park, PA 16802 USA
²The Aerospace Corporation, El Segundo, CA 90245 USA
³University of Texas - Austin, Austin, TX 78712 USA
⁴NASA-Marshall Space Flight Center, Huntsville, AL 35811 USA

Primary Technical Area: 14. Innovative Rocket Propulsion Techniques
Secondary Technical Area: 10. Test Methods and Diagnostic Techniques in Chemical Propulsion and/or Combustion of Energetic Materials

One of the most important factors currently preventing the practical use of hybrid rockets as boosters is the limited thrust level that can be generated from a simple port design. This limitation can be addressed either through a complex port geometry (with associated mechanical strength and fuel utilization issues) or by increasing the mass-burning rate of the oxidizer/fuel combination. A promising method to improve the regression rate of solid fuels used in hybrid rockets is to use a fuel with a high regression rate such as low melting point paraffin wax; however, additional increases to the fuel regression rate are necessary to make the fuel a viable candidate to replace current launch propulsion systems. Addition of energetic and/or nano-sized combustible particles can also increase mass-burning rates of the solid fuels and increase the overall performance of the hybrid rocket motor system.¹² Improving the mechanical properties of the paraffin wax is also important to produce more robust solid-fuel grains. This investigation studied the effect of various additives to paraffin wax burned with gaseous oxygen in a test rig called the Long-Grain Center-Perforated (LGCP) hybrid rocket motor. Shown in Figure 1, this lab-scale motor has been used for characterization of various oxidizer and fuel formulations.³

Several paraffin-based fuel grains with various energetic additives [e.g., lithium aluminum hydride (LiAlH₄) and cyclotrimethylenetrinitramine (RDX)] have been cast, and paraffin/LiAlH₄ fuel grains have been tested at representative oxidizer flux conditions. A major advantage of using LiAlH₄ as an additive to paraffin is the decreased dependency of $I_{sp}$ on oxidizer-to-fuel ratio. However, previous testing showed that continued work is necessary to eliminate deposition of unburned/unreacted fuel in downstream sections of the hybrid rocket motor.⁴ Changes to the fuel matrix include higher melting point wax and smaller (ball-milled) LiAlH₄ particles. With these changes, much more complete combustion was observed. Addition of LiAlH₄ at 10% by weight was found to increase regression rates between 7 – 10% over baseline paraffin. Mass burning rates were also higher.

Another promising fuel formulation consideration is to incorporate a small percentage of RDX as an additive to paraffin. A novel casting technique was used by dissolving RDX in a solvent (dimethylformamide) chosen for its compatibility with both paraffin and RDX, and combining the solution with the melted paraffin. The solvent was then evaporated out of the mixture, leaving the re-crystallized RDX dispersed in the paraffin. At low percentages of RDX additive and with RDX particles surrounded by paraffin, the fuel grains can remain inert, maintaining safety of the solid fuel. It was found that although all the solvent was removed, the process as currently applied was not conducive to generating small RDX particles. Neither rapid boiling nor slow removal of the
dimethylformamide produced particles of satisfactorily small size. Large particles were observed to settle in the melted paraffin wax, generating a non-homogeneous fuel grain structure.

One approach to improve mechanical properties of paraffin wax is with the addition of multi-walled carbon nanotubes (MWNT). For casting these solid-fuel grains, various percentages of MWNT were debulked via a sonication process similarly described in the literature and then added to the paraffin wax. The cost of MWNT is a small fraction of single-walled nanotubes. This is a scale-up advantage as future applications and projects will require low cost additives to maintain cost effectiveness. The fuel samples containing MWNT (up to 8%) showed good distribution of MWNT in the paraffin matrix, but the MWNT were often agglomerated, indicating that a change to the sonication and mixing processes were required to achieve better uniformity and debundled MWNT. Fuel grains with MWNT fuel grains had slightly lower regression rate, likely due to the increased thermal conductivity to the fuel subsurface, reducing the surface temperature.

![Figure 1. Photograph of LGCP hybrid rocket motor firing with a pure paraffin fuel grain manufactured by the Aerospace Corporation](image)

FORMULATION, CASTING, AND EVALUATION OF PARAFFIN-BASED SOLID FUELS CONTAINING ENERGETIC AND NOVEL ADDITIVES FOR HYBRID ROCKETS

Daniel B. Larson,1 John D. Desain,2 Eric Boyer,1 Trevor Wachs,1 Kenneth K. Kuo,1 Russell Borduin,3 Joseph H. Koo,3 Brian B. Brady,2 Thomas J. Curtiss,2 and George Story4

1 The Pennsylvania State University, University Park, PA 16802 USA
2 The Aerospace Corporation, El Segundo, CA 90245 USA
3 University of Texas - Austin, Austin, TX 78712 USA
4 NASA-Marshall Space Flight Center, Huntsville, AL 35811 USA

ABSTRACT

This investigation studied the inclusion of various additives to paraffin wax for use in a hybrid rocket motor. Some of the paraffin-based fuels were doped with various percentages of LiAlH4 (up to 10%). Addition of LiAlH4 at 10% was found to increase regression rates between 7 – 10% over baseline paraffin through tests in a gaseous oxygen hybrid rocket motor. Mass burn rates for paraffin grains with 10% LiAlH4 were also higher than those of the baseline paraffin. RDX was also cast into a paraffin sample via a novel casting process which involved dissolving RDX into dimethylformamide (DMF) solvent and then drawing a vacuum on the mixture of paraffin and RDX/DMF in order to evaporate out the DMF. It was found that although all DMF was removed, the process was not conducive to generating small RDX particles. The slow boiling generated an inhomogeneous mixture of paraffin and RDX. It is likely that superheating the DMF to cause rapid boiling would likely reduce RDX particle sizes. In addition to paraffin/LiAlH4 grains, multi-walled carbon nanotubes (MWNT) were cast in paraffin for testing in a hybrid rocket motor, and assorted samples containing a range of MWNT percentages in paraffin were imaged using SEM. The fuel samples showed good distribution of MWNT in the paraffin matrix, but the MWNT were often agglomerated, indicating that a change to the sonication and mixing processes were required to achieve better uniformity and debundled MWNT. Fuel grains with MWNT fuel grains had slightly lower regression rate, likely due to the increased thermal conductivity to the fuel subsurface, reducing the burning surface temperature.

INTRODUCTION

There are many advantages to hybrid rockets over solid and liquid rocket propulsion systems. One key advantage is safety. In contrast to a solid propellant, where the fuel and oxidizer are integrally mixed, a hybrid motor consists of an inert fuel and a separated oxidizer. This simple design contrasts with the complexity of liquid rocket systems. With an inert fuel, shipping and storage costs for hybrid fuels are significantly reduced, lowering overall cost. Hybrid fuels can also present lower environmental hazards due to exclusion of ammonium perchlorate (AP), which is commonly used as an oxidizer in solid propellants. This reduces impact on groundwater and the environment. A hybrid can also be throttled and has the potential
for stop and restart on demand. Although there are many benefits to using a hybrid rocket system, improved burning rates and mechanical strength would further raise the technology readiness level (TRL) of paraffin-fueled hybrid rockets.1 Paraffin wax-based solid fuels for use in hybrid rockets have shown regression rates which are far superior to conventional pyrolyzing fuels, with burn rates three to four times higher than HTPB.2,3 To further improve the mass burning rates of solid fuels, it is often useful to employ energetic and/or nano-sized particles. Hybrid rocket solid fuels with energetic or nano-sized particle additives have demonstrated significantly higher burning rates over baseline fuels.4,5

In an effort to improve the mass burn rates of hybrid rocket motors, the co-authors from the Aerospace Corporation have formulated and cast several solid-fuel grains containing lithium aluminum hydride (LiAlH₄ or LAH). The LiAlH₄ fuel grains have shown the ability to ignite with strong acids, demonstrating the potential for restart on demand with a simple ignition method. The reaction of the paraffin fuel (C₃₂H₆₆) doped with LiAlH₄ to strong acids (e.g., nitric acid) was found to be hypergolic.6,7 A key benefit of using LiAlH₄ in paraffin wax are reduced dependency of specific impulse (Iₚ) on oxidizer-to-fuel ratio. The LiAlH₄ addition allows for system operation through a wider range oxidizer-to-fuel ratio (O/F) while remaining close to peak Iₚ. This benefit is shown in Fig. 1. Addition of LiAlH₄ to paraffin also increased theoretical characteristic velocity. Previous tests on solid-fuel grains revealed that a change in to the fuel matrix (i.e., higher melting point fuel and smaller LiAlH₄ particles) might help to reduce the amount of unburned fuel which was accumulating in downstream sections of the hybrid motor (up to 22% of mass lost).8 Smaller (ball-milled) LiAlH₄ particles have been found to dehydrogenate more rapidly, the first step in the decomposition reaction of LiAlH₄.9

Figure 1. Thermochemical calculations of Iₚ for various percentages of LiAlH₄ in paraffin wax (calculated for chamber pressure of 6.9 MPa with a nozzle expansion ratio of 10)
Cyclotrimethylenetritramine (C₃H₆N₆O₆), commonly known as RDX, is another additive with the potential to increase bulk density as well as improve the mass burning rates of paraffin. With a density of 1.82 g/cm³, RDX is around twice the density of paraffin wax. In addition to increasing the bulk density of the hybrid fuel, RDX may also increase the mass burn rates of the fuel, because it is an energetic material. RDX is a familiar ingredient in rocket and high-energy gun propellants. A novel casting technique of dissolving RDX in a solvent which is compatible with paraffin wax could produce well-dispersed particles of RDX embedded in a paraffin fuel matrix.

Inclusion of RDX in low percentages (< 15%) would keep the solid-fuel grain effectively inert. A DOT Class 1.4C rating was given to fuel-rich propellant formulations containing 60% AP in an HTPB/PPG binder for use in a hybrid rocket. Keeping the fuel grain relatively inert with a hazard classification below 1.3 is essential to maintaining the overall safety and operability advantages of the hybrid system. Thermal and stability behavior of RDX is well known and documented. RDX is soluble in various solvents such as acetone and dimethylformamide (C₃H₇NO), and the solubility data has been extensively documented.13 Once the RDX is dissolved in the solvent, the solvent can be boiled out of the melted paraffin. The boiling point of dimethylformamide (DMF) is high (~153 °C), but a vacuum can be drawn to lower the boiling point of the DMF to a value closer to the melting point of paraffin wax.14 In this study, DMF was selected due to its high solubility of RDX with boiling point higher than the casting temperature of paraffin wax at atmospheric pressure and a boiling point below the paraffin casting temperature at sub-atmospheric pressures.

Along with increasing bulk density and regression rate, the mechanical properties of paraffin can be improved to provide more robust solid-fuel grains. Mechanical properties of paraffin-based solid fuel have been tested and published. The inclusion of multi-walled carbon nanotubes (MWNT) has the potential to improve mechanical properties and change the burn rate of paraffin wax. Prior to this study, MWNT have been added to paraffin wax and tested for thermal performance. These samples showed an increase in thermal conductivity as MWNT additive amount increased. Mixing procedures for distributing multi-walled carbon nanotubes in polymers as well as a phenolic resin for ablative applications have also been documented in the literature. MWNT are much lower cost compared to single-walled nanotubes. Due to the mechanical strength advantageous and low cost, MWNT were selected as an additive to paraffin wax to determine mechanical property benefits and changes in regression rate.

**METHOD OF APPROACH**

Work presented in this paper occurred in several phases. The Aerospace Corporation ball milled LiAlH₄ and cast paraffin-based fuel grains with various percentages of LiAlH₄. Solid-fuel grains were also cast at the High Pressure Combustion Lab (HPCL) at the Pennsylvania State University (PSU). Solid-fuel grain samples which were processed at the HPCL included RDX and MWNT additives in paraffin. The paraffin wax with MWNT samples were sent to the Center for Nano and Molecular Science and Technology at University of Texas—Austin for TGA and SEM analysis. Along with these small (~50 gram) samples of solid fuel for thermal analysis, hybrid rocket fuel grains were also manufactured for test firings. All types of solid-fuel grains produced either at the Aerospace Corporation or at PSU were tested in a hybrid rocket system at PSU.
LiAlH$_4$ Casting

In order to reduce LiAlH$_4$ particle size, the coauthors from the Aerospace Corporation used a ball milling technique. Because LiAlH$_4$ is reactive with water, it must be kept in a nitrogen environment as much as possible. LiAlH$_4$ particles were ball milled for various amounts of time and examined using SEM techniques. Particles milled for 300 hours were cast into paraffin wax with a melting point between 70 and 80 °C. This was performed by melting the wax and mixing the additives before pouring into a paper phenolic tube held inside an aluminum mold. The paper phenolic tube, which serves as the hybrid rocket motor solid-fuel cartridge, has an outer diameter of 1.5 inches (3.81 cm), an inner diameter of 1.25 inches (3.175 cm), and was cut to 16-inch (40.64-cm) lengths to fit inside the aluminum mold. Once wax was poured into the mold, it was spun on a lathe to bond the solid fuel to the case wall, because the wax shrinks during cooling. These steps were repeated for multiple pours to fill the fuel grain cartridge. After each grain had solidified, a center port between 0.35 and 0.51 inches (0.889 and 1.295 cm) was cut, and the grain was cut to lengths of 4, 5, and 5.5 inches (10.16, 12.7, and 13.97 cm) in order to maintain desirable combustion O/F ratios at the three different oxidizer flux levels tested.

RDX Casting

Before casting full-size fuel grains for use in an HPCL hybrid rocket motor, 50 gram samples consisting of 4 wt% of RDX and 96 wt% of paraffin were generated. Wetted, Class I, Type II military grade RDX was measured and baked at low temperature in order to dry out the RDX powder. The RDX powder was then weighed again, and dissolved in approximately 15 mL of dimethylformamide. Once dissolved, the DMF/RDX solution could safely be transferred to the casting chamber, where paraffin wax had been melted and held at around 100 °C. The heating and mixing setup is shown in Fig. 2. It should be noted that all mixer clearances were checked to avoid contact with the mixing bowl and equipment was grounded in accordance with DoD standards. With the mixer turned on, the DMF/RDX solution was poured into the melted paraffin. The environmental chamber door was then closed, and a camera with a live feed was placed near the window, so that the casting process could be monitored remotely.

![Figure 2. Solid fuel casting setup in vacuum chamber](image-url)
The chamber was then pumped down to approximately 4 psia (27.6 kPa), where the boiling point of the DMF is around 110 °C. The paraffin temperature was raised to above this value, so that the DMF could boil out slowly, allowing RDX to nucleate out of the supersaturated DMF/RDX solution. After approximately 1.5 hours of continuous mixing, a vacuum was slowly drawn down to ~1 psia (6.9 kPa) to check for bubbling from any remaining DMF. When there was no boiling of DMF, this indicated that no DMF remained in the mixture. The chamber was then pressurized, heating equipment was turned off, and mixing was stopped. Photographs of the liquid paraffin mixture with suspended RDX particles were taken before the paraffin cooled, to check for the dispersion status of RDX particles.

MWNT Casting

Casting of MWNT occurred in several steps. In order to evenly disperse the MWNT in paraffin and take advantage of their small size, the MWNT must be debulked. This is typically done by sonicating the MWNT in a solvent and then removing the solvent from the final material. In this study, the MWNT were sonicated in toluene. The typical ratio of MWNT to toluene was between 1 and 2 grams per 100 mL of toluene. The sonication process was limited to approximately 20 minutes, as toluene has been observed to break down if sonicated intensely or for long periods of time. Because toluene’s boiling point is around 110 °C, the paraffin can be heated slowly until it is above toluene’s boiling point and held at that temperature until the toluene is fully removed.

After sonicating the toluene/MWNT mixture and adding it to paraffin held at around 100 °C, the environmental chamber door was closed, with a vent line to atmosphere. Due to toluene’s flammability in air, the environmental chamber was constantly purged with nitrogen during the mixing process until the toluene was removed. A fan was also used on the interior of the environmental chamber to promote circulation of the dense toluene vapors. Small scale batches of 50 grams were generated with various MWNT additive amounts ranging from 0 to 8% MWNT. These small scale samples were sent to the Center for Nano and Molecular Science and Technology at University of Texas—Austin for DSC, TGA, and SEM testing.

A fuel grain for testing in a hybrid rocket motor was also generated. The formulation for this grain was 4 wt% MWNT in paraffin wax. Instead of using an aluminum mold to seal the paraffin inside the phenolic fuel cartridge, PSU’s casting process used end caps on the phenolic fuel cartridge. The grain was spun on a lathe at approximately 400 rpm and then reheated in an oven to soften the wax before the next pour. This was performed to generate better bonding between poured layers and good adhesion of the fuel to the case wall. The grains were then cut to 4.5-inch (11.43-cm) lengths.

Hybrid Rocket Motor Test Setup

The hybrid rocket motor used to evaluate the solid-fuel grains in this study is called the Long Grain Center Perforated (LGCP) hybrid rocket motor. It allows for fuel grains with lengths up to 16 inches (40.64 cm) and has an inner diameter of 1.5 inches (3.81 cm). Using graphite inserts as volume-filling spacers, fuel lengths can be varied significantly to control fuel burning surface area. The LGCP system is shown in Fig. 4. In these experiments, desired pressures were typically between 200 and 350 psia (1.38 MPa and 2.41 MPa), depending on nozzle size. The small size of the LGCP and fast turnaround times during testing make it an ideal motor for
testing new fuel formulations, while consuming a minimal amount of fuel. The LGCP ran with
gaseous oxygen and with a nitrogen purge for this test matrix, but the LGCP can accommodate
other oxidizers such as nitrous oxide.

Figure 4. Schematic diagram of long grain center perforated (LGCP) hybrid rocket motor
setup

The results from the LGCP motor firings are best for comparing different formulations of
solid fuel because of the relatively thin fuel web and resulting short burn duration for high-
regression rate fuel formulations. Equations (1) and (2) were used in developing plots of
regression rate versus oxidizer mass flux. 20 \( D_i \) and \( D_f \) are initial and final fuel grain port
diameters respectively, and \( t_b \) is the burn time. Final port diameter (\( D_f \)) is often found by
measuring in several places at the fore and aft end of the fuel grain after firing, but in the case of
this study Eq. (3) is used. This relies on accurate measurements of grain mass and fuel density
rather than center port diameters measured along the length of the post-fired fuel grain. In Eq.
(3), \( M_i \) and \( M_f \) are the initial and final mass of the solid fuel, respectively.

\[
\overline{\mathbf{r}} \cong \frac{D_f - D_i}{2t_b} \quad (1)
\]

\[
\overline{G}_{ox} = \frac{16\overline{h_{ox}}}{\pi(D_f + D_i)^2} \quad (2)
\]

\[
D_f = \sqrt{D_i^2 + \frac{4(M_i - M_f)}{\pi L_{fuel}}} \quad (3)
\]
RESULTS AND DISCUSSION

LiAlH₄ Casting Results

The LiAlH₄ ball milling process successfully reduced the particle sizes. As shown in Fig. 5, SEM images of the LiAlH₄ particles reveal that after 300 hours, the particles are generally sub-micron size, with many particles less than 100 nm. However, many of the particles have an alumina layer which would delay the decomposition of the particles during combustion. With these smaller particles, the LiAlH₄ was successfully mixed into a high melting point (70 to 80 °C) paraffin wax and cast in phenolic cartriges for testing in the LGCP hybrid rocket motor. Upon cutting the solid fuel grains prior to testing, the fuel grains appeared homogeneous with few voids or defects. Although center port diameter varied, the grains were deemed usable for hybrid rocket motor tests after measuring average mass and center port diameter.

Figure 5. SEM images of LiAlH₄ particles after a) 3 hours, b) 35 hours, and c) 300 hours of ball milling

RDX Casting Results

A sample batch of paraffin/RDX fuel was cast with 48 grams of paraffin and 2 grams of RDX in approximately 15 mL of dimethylformamide. After following the procedure outlined in the “Method of Approach” section, the RDX particles were observed and photographed before allowing the melted paraffin to solidify. One of these images is shown in Fig. 6.
As shown in Fig. 6, the RDX particles nucleated out of the DMF, but the size of the particles is large, and the dispersion of the particles in the melted paraffin was poor. Because the DMF was evaporated out of the paraffin slowly, it allowed DMF/RDX solution to become only slightly supersaturated over time. This is visible in Fig. 7 (generated from Antoine equation parameters\textsuperscript{14}), as “Cast Condition 2.” This slow boiling process resulted in large RDX particles. In order to reduce the particle size, one possible route is to decrease the boiling time, by dropping the pressure in the vacuum chamber to bring the DMF to a significantly superheated state, causing rapid boiling. However, in an earlier attempt to boil off the DMF (“Cast Condition 1” in Fig. 7), the pressure in the chamber was reduced to a point where the boiling point of the DMF was 20 to 30 °C below the temperature of the paraffin, causing undesirable violent boiling of DMF due to superheating. To generate small particles, without violent boiling, a median approach must be used. The DMF must be allowed to bubble and boil rapidly, but not to the point where it becomes a violent reaction.
MWNT Casting Results

Throughout the cast processes for various samples of paraffin wax containing different concentrations of MWNT, it was noted that higher weight percentages of MWNT caused a significant increase in the viscosity of the melted fuel. In addition, at higher concentrations of MWNT, sonication became more difficult as large volumes of toluene were required. For example, to debulk enough MWNT necessary to generate one solid fuel grain for testing in the LGCP hybrid rocket motor, approximately 1.5 L of toluene was used during sonication. Even with this large amount of toluene, after sonication, and after pouring the wax into the hybrid rocket motor, there was a large amount of settled nanotubes. The agglomeration of the nanotubes inside of the paraffin wax can be seen in Fig. 8, with two different samples. It should be noted that when 4 wt% MWNT or 8 wt% MWNT is stated, this corresponds to the amount initially added to the toluene prior to sonicating; it is likely that the total concentration of nanotubes in the mixture is lower than the stated value. This is due to losses in the casting process (i.e. nanotubes getting stuck to mixer bowl, beakers, mixing blades, etc).
Figure 8. SEM images of broken surfaces of paraffin wax with a) 4 wt% MWNT and b) 8 wt% MWNT showing dispersed MWNT but with local clumping

In the images above, surface charge buildup appears as local bright spots. In order to reduce the amount of surface charge buildup and improve image quality, the sample shown in Fig. 9 was sputter coated with gold and palladium particles. This close-up image, with improved image quality, is of a fuel sample containing 8 wt% MWNT in paraffin wax.

Figure 9. Close-up SEM image of paraffin fuel sample with 8 wt% MWNT, coated with gold and palladium for better image quality and reduced surface charge buildup

It can be seen in Fig. 9 that the MWNT (light colored strings) appear bundled in most areas. There is still some charge buildup on the surface of the sample. The bundling of MWNT is most likely due to stirring of the paraffin/toluene/MWNT mixture while toluene is boiled out. This stirring can take several hours before toluene is fully removed. Another possibility is that
the MWNT are not fully dispersed in toluene during sonication, because sonication time is limited by toluene breakdown. Therefore, the use of a wand-type sonicator to simply sonicate the MWNT in the paraffin is required. This could provide good mixing of the MWNT and also debulk the nanotubes in the process, while eliminating the need for toluene.

**Hybrid Rocket Motor Test Results**

Various fuel formulations were tested in the LGCP hybrid rocket motor in this study, including different pure paraffin formulations as baselines, 4 wt% MWNT in paraffin, 5 wt% LiAlH$_4$ in paraffin, and 10 wt% LiAlH$_4$ in paraffin. A photograph of an LGCP motor firing is shown in Fig 10.

![Photograph of LGCP hybrid rocket motor tested with a pure paraffin fuel grain manufactured by the Aerospace Corporation.](image)

**Figure 10.** Photograph of LGCP hybrid rocket motor tested with a pure paraffin fuel grain manufactured by the Aerospace Corporation.

In a previous study conducted by PSU and the Aerospace Corporation team members, non-negligible amounts of LiAlH$_4$ in paraffin wax were deposited in the downstream sections of the hybrid rocket setup (i.e., graphite transition section and nozzle). Due to these accumulations, the tests were run at similar conditions, with initial oxidizer mass fluxes of approximately 220 kg/m$^2$-s with chamber pressures typically between 150 and 250 psig (1.03 and 1.72 MPa). In this test series, the amount of deposited fuel on the downstream sections of the hybrid rocket motor was found to be negligible. There was still a thin film of particles which thinly coated the inside of the transition section, but it was not an appreciable mass. However, upon submerging the transition section in water, it was found to bubble slowly. This indicated that some form of LiAlH$_4$ was still unreacted in the downstream components of the motor, since LiAlH$_4$ is highly reactive with water. A set of typical pressure-time traces is given in Fig. 11.
Figure 11. Typical set of pressure-time traces from hybrid rocket motor firing (gaseous oxygen with 10% LiAlH$_4$ in paraffin wax) with an O/F $\approx$ 2.1

The pressure-time traces shown in Fig. 11 are indicative of a typical motor firing with steady burning behavior. Ignition takes place just after time = 0, and combustion terminates at approximately 1.9 seconds. The average chamber head pressure during steady state burning was 245 psig (1.69 MPa). It is important to note that after the oxygen run valve closes, there is a slight drop in oxygen before upstream nitrogen forces a check valve closed. Nitrogen purge gas was set at higher pressure than the O$_2$ pressure upstream of the orifice, in order to close this check valve. Due to the higher pressure, the N$_2$ purge gas overdrives the oxygen into the chamber, although there is little appreciable effect in the O$_2$ pressure downstream of the orifice. Because the HPCL hybrid facility was originally designed for motors with flow rates up to 360 g/s, many of the valve locations make fast start-up and shut-down timing problematic. Relocation of check valves and overdriving O$_2$ pressure with nitrogen to extinguish combustion addressed these issues. In order to determine the mass flow rate of oxygen, the average upstream pressure (top pressure trace in Fig. 11) from ignition to burnout was used. In general, this value was not appreciably affected by the overdrive from nitrogen.

Because the LGCP hybrid rocket motor is used more to determine regression comparisons, the delay in ball valve timing and motor shutoff is not particularly significant. For accurate regression rate calculations, a larger diameter, X-ray transparent hybrid rocket motor is used to obtain instantaneous, real-time regression rate values over longer burn times. A comparison of useable tests from the LGCP is shown below in Fig 12. Since the final port diameter (D$_f$), described in the “Method of Approach” section, was based on fuel density, it is important to note that the density of LiAlH$_4$ additive fuels was measured to be 0.86 g/cm$^3$, the density of the Aerospace Corporation’s pure paraffin grains was taken as 0.898 g/cm$^3$, PSU’s pure paraffin was taken as 0.86 g/cm$^3$, and PSU’s MWNT additive grains were 0.865 g/cm$^3$. It
was noted that on several grains, there was some end burning between the case wall and the fuel. This would affect data by causing the calculated $D_f$ to be larger than would typically be found. However, when comparing calculated $D_f$ to measured $D_f$, the values were typically within 10% of one another.

![Figure 12](image)

**Figure 12.** Plot of deduced regression rates for various paraffin-based solid fuels tested with gaseous oxygen (* Fuel grains run at lower O/F than the others plotted at O/F ratios between 2.0 and 2.4)*

It can be seen from the regression rate comparison plot (Fig. 12) that the Aerospace Corporation paraffin/10% LiAlH$_4$ fuel grains had a slightly higher regression rate than the pure paraffin fuel grains manufactured by the Aerospace Corporation. The LiAlH$_4$/paraffin shows approximately a 7 – 10% increase over the pure paraffin wax between average oxidizer mass flux values of 60 and 100 kg/m$^2$-s. Some of this increase in regression rate could be due to the slightly lower measured density of LiAlH$_4$-doped paraffin fuel; however, as shown in Fig. 13, mass burn rates for paraffin/10% LiAlH$_4$ fuel grains are still higher than the baseline paraffin grains. The PSU paraffin has an uncharacteristically high regression rate, which is explained by the low density that was measured from the fuel grains. When compared in Fig. 13, PSU’s baseline paraffin had only slightly higher mass burn rates than the Aerospace paraffin. Low
density grains have the tendency to burn faster. This is indicative of casting procedures which allow for the paraffin to keep air in the fuel matrix or simply the grade of paraffin used. This likely occurs after spinning on the lathe and reheating prior to the subsequent pour. Either the pour temperature is too low, or the heat soak (prior to pouring the second layer) is not deep enough, and surface bubbles and imperfections are not melted away.

It should also be noted from the regression rate graph (Fig. 12) that formulations marked with a “*” in Fig. were labeled as such because they were run at lower O/F ratios (1.5 – 1.75). It was expected that fuel grains containing 4% MWNT would have slightly reduced burn rates due to the amount of graphite in the grain. MWNT increase conductivity to the subsurface layers of the fuel grain, possibly reducing the surface temperature of the burning fuel, resulting in decreased regression rate. Although the regression rate was slightly slower, it is possible that the MWNT could replace carbon black or chemical dies in fuel grain formulations, providing the same radiation heat transfer benefits of stopping any subsurface reaction, while also delivering improved mechanical properties. The inclusion of energetic additives in addition to MWNT is another possibility to improve both the mechanical properties of the paraffin and the mass burn rate and density. Addition of MWNT to the fuel grain would tend to reduce the overall density of the solid-fuel grains due to the lower density of carbon compared to paraffin wax.

![Graph](image_url)

**Figure 13.** Plot of deduced mass burn rates for various paraffin-based solid fuels tested with gaseous oxygen (* Fuel grains run at lower O/F than the others plotted at O/F ratios between 2.0 and 2.4)
If not otherwise noted in Fig. 12 and Fig. 13, and aside from one test where fuel grain which burned into the phenolic cartridge wall (5% LiAlH₄), all other tests were run with O/F values between around 2 to 2.4. For the Aerospace Corporation manufactured grains, the O/F for the pure paraffin tests was around 2.3 to 2.4, while the O/F for the grains doped with 10% LiAlH₄ was between 2 and 2.2. This is satisfactory because, as shown in Fig. 1, peak Iₚ for 10% LiAlH₄ occurs at a slightly lower O/F value than for pure paraffin. Regression rate data in Fig. 11 also supports previous assertions that increases in LiAlH₄ additive allow a hybrid rocket to run at lower O/F ranges than pure paraffin without sacrificing Iₚ. This is most clear when looking at the data points from pure Aerospace Corporation paraffin and 10% LiAlH₄ which show a regression rate of ~2.6 mm/s. The 10% LiAlH₄ paraffin was run at lower oxidizer mass flux, but achieve the same regression rate. It can be concluded that increases in LiAlH₄ content can improve regression rate of the paraffin fuel; however, the described tests are a limited test sequence. In order to achieve a more complete test matrix, fuel grains containing 15-25% sub-micron LiAlH₄ could be processed and tested to better observe the effect of this beneficial additive. Load cell data was not conclusive when analyzed for large differences in thrust between the LiAlH₄/paraffin motors compared to pure paraffin motors. This was because chamber pressures between LiAlH₄-doped paraffin and pure paraffin fuel grains were very similar. Chamber pressures between the two tests at each condition were within 5% of each other.

**SUMMARY AND CONCLUSIONS**

1) LiAlH₄ particle size was significantly reduced over 300 hours of ball milling and fuel grains with 0, 5, and 10 wt% of LiAlH₄ showed excellent homogeneity. Examination of the post-fired samples of the paraffin fuel grains with LiAlH₄ revealed highly uniform center port geometry.

2) A 10 wt% addition of LiAlH₄ to paraffin wax showed a 7 – 10% increase in regression rate over that of the baseline paraffin fuel cast by Aerospace Corporation, although part of this increase in burn rate is likely due to lower density of the LiAlH₄-doped paraffin wax compared to pure paraffin. Mass burn rate comparisons confirmed a burn rate increase for grains doped with LiAlH₄ over pure paraffin.

3) Solid-fuel samples with MWNT were imaged using an SEM, and revealed uniform MWNT distribution, although the MWNT were often clumped together. Changes to the casting procedure are required to better disperse the MWNT in the paraffin. The paraffin/4 wt% MWNT fired in the LGCP hybrid rocket motor demonstrated consistent burning, although regression rate was slightly lower than the baseline PSU paraffin fuel. This reduction in regression rate is believed to be caused by the increase in thermal conductivity of the solid fuel with MWNT additives. When the energy transfer to the subsurface region is faster, the fuel surface temperature may be reduced, therefore resulting in reduced mass burning rates.

4) A novel RDX/paraffin casting procedure was developed and demonstrated. RDX particles nucleating out of the dimethylformamide/RDX solution were too large, likely due to a slow boiling process. Improvements to the process were identified to achieve more uniform properties in paraffin wax.
Future Work

1) Additional testing is planned for test firings with paraffin fuels containing 20 wt% LiAlH4, in order to generate more systematic data to better characterize the enhancement of regression by this energetic additive.

2) Cast new grains for use in a larger hybrid rocket motor system at PSU’s High Pressure Combustion Lab. The X-ray Transparent Center-perforated (XTC) hybrid rocket motor allows for real time regression analysis which is far more accurate in determining regression rates for various fuel formulations.

3) Cast new batches of RDX with smaller, more evenly distributed particles in the paraffin matrix by drawing a deeper vacuum to cause supersaturation of RDX in the boiling dimethylformamide solvent.

4) Create paraffin/MWNT samples for mechanical testing at the University of Texas—Austin. Also, cast new grains with carbon black to compare with similar percentages of MWNT.

ACKNOWLEDGEMENTS

This work was supported (in part) by a NASA Office of the Chief Technologist’s Space Technology Research Fellowship for Daniel Larson’s M.S. program.

REFERENCES

Formulation, Casting, and Evaluation of Paraffin-Based Solid Fuels Containing Energetic and Novel Additives for Hybrid Rockets

Daniel B. Larson, Eric Boyer, Trevor Wachs, and Kenneth K. Kuo
The Pennsylvania State University, University Park, PA 16802

John D. DeSain, Thomas J. Curtiss, and Brian B. Brady
The Aerospace Corporation, El Segundo, CA 90245

Russell Borduin and Joseph H. Koo
University of Texas—Austin, Austin, TX 78712
And

George Story
NASA-Marshall Space Flight Center, Huntsville, AL 35811

9th International Symposium on Special Topics in Chemical Propulsion
July 2012

The Pennsylvania State University The Aerospace Corporation
Introduction

• Three solid-fuel additives considered for use in paraffin fuel in hybrid rocket system burning with gaseous O$_2$:
  – Lithium Aluminum Hydride {LAH or LiAlH$_4$}
    • LiAlH$_4$ shown to be pyrophoric with strong acids (e.g., nitric acid)
    • Restart on demand without replacement igniters
    • Fuel grains manufactured at the Aerospace Corporation
  – Cyclotrimethylenetrinitramine {RDX or C$_3$H$_6$N$_6$O$_6$}
    • Energetic additive with potential to increase density specific impulse
  – Multi-Walled Carbon Nanotubes {MWNT}
    • Potential to increase mechanical properties
• Solid-fuel grains tested in a hybrid rocket motor at PSU’s High Pressure Combustion Laboratory (HPCL)
Hybrid rocket pros and cons

Advantages:
• Improved safety
• Robustness
• Environmental impact
• Low cost

Disadvantages:
• Low bulk density
• Low regression rate
• O/F shift

Kuo and Chiaverini, 2005
Thermochemical calculations: $I_{sp}$ vs. O/F

Larson, et al., 2011

Theoretical Specific Impulse ($I_{sp}$), s

Increasing Percentage of LiAlH$_4$

Chamber pressure = 6.9 MPa, Nozzle Expansion Ratio = 10
Pressure-time traces for various additives

Larson, et al., 2011

Ignition at time = 0 s and tests at initial O₂ fluxes of ~220 kg/m²-s
Fuel deposits in downstream sections of hybrid rocket motor

- Observed deposition of unburned/unreacted fuel from hybrid motor firings
  - Typical results showed several grams of accumulation in downstream sections
  - 10% - 22% of fuel trapped downstream
- LiAlH$_4$ particles may have been too large
- Particles may have been getting trapped in wax and carried downstream
  - Higher melting point wax may allow more complete LiAlH$_4$ particle reaction due to higher temperatures near burning fuel surface
    - Thinner melt layer

Larson, et al., 2011
Solid-fuel grain characteristics

Desirable Features:
- Homogeneous grain structure
- High repeatability
  - P-t trace data
  - Consumption rate
- Uniform surface burning
- Complete combustion
- High regression rate
- Structure integrity

Undesirable Features:
- Voids in grain
- Deposition of fuel in downstream components
  - Unreacted additive particles
- Grain delamination prior to or during burn
- Uneven burning
- Low regression rate
- Poor mechanical properties
Ball-milled LiAlH$_4$ particles

- Majority of particles less than 100 nm after 300 hours
- Many particles have alumina layer
  - Could delay or inhibit combustion/particle decomposition
Aerospace Corp. fuel grain casting

- Wax melted in beaker
  - LiAlH\(_4\) addition occurred in N\(_2\)-purged bag
- Mixture was poured into phenolic tube through filling ports on wax motor mold
  - Spun on lathe @ 400 RPM
- Grains cast in 3 poured layers
- Grains were perforated with a 3/8-inch hole and cut to various lengths
PSU fuel grain casting

- Wax melted in mixing pot
- Environmental chamber can be used with $N_2$ purge or vacuum pump
  - MWNT with nitrogen
  - RDX with vacuum
- Spun on lathe @ 400 RPM
- Grains cast in 2 poured layers
- Grains were perforated with a 3/8-inch hole and cut to various lengths
Paraffin/RDX fuel sample casting

![Graph showing the relationship between pressure (kPa) and temperature (°C) with different conditions.]

- **DMF Boiling Point**
- **Paraffin Melting Point**
- **Paraffin Casting Temp**

**Cast Conditions:**
- Cast Condition 1
- Cast Condition 2
- Cast Condition 3

The Pennsylvania State University

The Aerospace Corporation
RDX fuel sample casting result

Collection of RDX particles around edges of mixture

Local accumulation of RDX particles suspended in paraffin

~ 13 cm
Paraffin/MWNT fuel casting

- MWNT measured and mixed with toluene
  - (100mL toluene / 1-2 grams MWNT)
- Beaker floated in water sonication bath and sonicated for ~20 mins
- Mixture transferred to melted paraffin (held at < 110 °C)
- Environmental chamber door closed, nitrogen purge gas flow started
- Paraffin temperature increased above BP of toluene
- Mixed until complete removal of toluene
- Various small fuel samples (<50 grams) sent to Center for Nano and Molecular Science at University of Texas—Austin for TGA, DSC, and SEM tests
  - 0% - 8% MWNT concentrations
- One solid-fuel grain (paraffin/4% MWNT) cast for testing in hybrid rocket motor
Paraffin/MWNT fuel samples

Increasing SEM magnification from 1mm to 100 μm for paraffin/4% MWNT sample
Paraffin/MWNT fuel samples

- 8% MWNT with uncoated (left) and coated (right) surfaces
- MWNT is well distributed, but clumped together
Hybrid rocket motor firings

Long-Grain Center-Perforated (LGCP) hybrid rocket motor:
- Cartridge load system for a paper phenolic tube with 38.1-mm (1.5") diameter and length of 406.4 mm (16")
- Chamber pressures up to 12 MPa (1,750 psi)
- O₂ mass flow rates up to 0.36 kg/s (0.8 lbm/s)
  - Tests in this study:
    - Pressure max was ~3.2 MPa (~465 psi)
    - O₂ mass flow rates between 20 and 54 g/s (0.044 – 0.119 lbm/s)
    - Average O₂ flux (G₀ₓ) values between 49 and 115 kg/m²-s
- Four pressure transducers (2 on feed system and 2 chamber), load cell, data acquisition system and live video feed for recording tests
Long-Grain Center-Perforated Hybrid Rocket Motor

Grain Length = 16 inches
Grain Diameter = 1.25 inches
Typical videos of motor firings

- Pure Paraffin
- Paraffin/LiAlH₄
- Paraffin/MWNT
Pressure-time traces from paraffin fuel grain containing 10% LiAlH₄
Regression rates of various solid-fuel formulations

The Pennsylvania State University

The Aerospace Corporation
Mass burning rates of various solid-fuel formulations

![Graph showing average mass burn rate vs. average oxidizer mass flux for different fuel formulations.]

- **Aero Paraffin**
- **PSU Paraffin**
- **PSU Paraffin**
- **4% MWNT**
- **5% LAH**
- **10% LAH**

Burned to cartridge wall
Broken Transition Section/Blocked Nozzle
Broken Transition Section/Blocked Nozzle

The Pennsylvania State University
The Aerospace Corporation
Conclusions

- Ball-milled LiAlH\textsubscript{4} particle sizes were much smaller and fuel grains with LiAlH\textsubscript{4} were very homogeneous
  - Post firing grain geometry was also highly uniform
- 10\% LiAlH\textsubscript{4} in paraffin showed 7-10\% increase in regression rate over baseline paraffin (some increase due to lower density)
  - 10\% LiAlH\textsubscript{4} fuel grain also had higher mass burn rates
- Casts with MWNT showed good distribution, but MWNT were often bundled together
  - Fuel grain with 4\% MWNT had slightly reduced regression rates, possibly due to increase in thermal conductivity
- RDX particles cast into paraffin wax using several casting methods were too large to produce fuel grain for hybrid testing
  - Safe procedure developed, but more work with RDX/DMF/Paraffin solubility limits is required
Future work

• Continue testing Paraffin/LiAlH$_4$ fuel grains with higher LiAlH$_4$ concentrations (15 – 25%)
• Cast new grains for use in the larger hybrid system at PSU’s High Pressure Combustion Lab
  – X-ray Translucent Center-perforated (XTC)
    o Larger system means thicker web for longer burn
    o X-ray diagnostics are conducive to accurate instantaneous fuel regression rate assessment
• Create Paraffin/MWNT samples for mechanical testing at University of Texas-Austin
• Generate fuel grains with carbon black in same percentage of MWNT to compare burn rates
• Carry out additional experiments on solubility limits of RDX/DMF/paraffin to achieve a uniform mixture with small RDX particles uniformly dispersed in the paraffin wax matrix
Questions?