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Detailed Characterization of Al/Ice Propellants

Timothée L. Pourpoint[1], Travis R. Sippel[2], Chris Zaseck[3], Tyler D. Wood[4], and Steven F. Son[5]
Purdue University, West Lafayette, IN, 47907, USA

Grant A. Risha[6] and Richard A. Yetter[7]
The Pennsylvania State University, University Park, PA, 16802, USA

Several experimental and theoretical studies over the last few decades have addressed the aluminum-water reaction. Practical applications making use of the heat generated and the products of the aluminum water reaction can be grouped into two main categories: power generation and propulsion. Power generation is typically achieved by feeding the hydrogen produced into a fuel cell. In propulsion applications, the products of the reaction burn at high pressure and are expelled at high velocity through a converging/diverging nozzle. With a focus on propulsion applications, we presented in a previous paper the results of nano-aluminum/ice (ALICE) small-scale static experiments. We showed that ALICE mixtures are stable, as well as insensitive to electrostatic discharge, impact and shock. Since then, a sounding rocket was successfully launched, powered by the ALICE propellant; the first time a propellant of this type has been flown. Although this formulation is not a practical formulation, the flight established a stepping stone for better performing propellant mixtures. Hydrogen peroxide and micron aluminum mixtures are under development and have shown promise to improve performance. Additional characterization with several nano energetic materials and bi-modal mixtures is also reported.

Nomenclature

a, n	=	propellant burning rate coefficients
A_b	=	burning area
A_t	=	throat area
c^*	=	characteristic velocity
Isp	=	specific impulse
$\dot{m}$	=	mass flow rate
P_c	=	chamber pressure
r_b	=	burning rate
ε	=	thickness of alumina deposit
ρ_p	=	propellant density
γ	=	specific heat ratio

Subscript

i	=	inner
in	=	inlet
o	=	outer
out	=	outlet

[1] Research Assistant Professor, Aeronautics & Astronautics, Purdue University, Senior AIAA Member
[2] Graduate Student, Mechanical Engineering, Purdue University, AIAA Member
[3] Graduate Student, Aeronautics & Astronautics Engineering, Purdue University, AIAA Member
[4] Graduate Student, Mechanical Engineering, Purdue University, AIAA Member
[5] Associate Professor, Mechanical Engineering and Aeronautics & Astronautics (courtesy), Purdue University, AIAA Member
[6] Assistant Professor, Division of Business and Engineering, The Pennsylvania State University, Altoona College, AIAA Member
[7] Professor, Mechanical Engineering, The Pennsylvania State University, AIAA Member

I. Introduction

ALUMINUM and water propellants have shown promise in eliminating some of the disadvantages of AP-based propellants, yet present many challenges also. Theoretical calculations with aluminum-water mixtures by Ingenito et al. predict a vacuum specific impulse (Isp_{vac}) of over 300 s [1]. The aluminum and water propellant have an environmental benefit as well. Aluminum oxide (Al_2O_3 or alumina) and hydrogen gas are the major products of the combustion process, resulting in a more environmentally friendly propellant [2,3]. Freezing the aluminum-water propellant has been shown to prolong the life of the propellant, potentially eliminating aging issues [4]. Furthermore, aluminum and water propellants are theorized to be well-suited for deep space exploration because the propellant could potentially be formed in situ. Research has shown that the abundance of aluminum within the lunar crust is similar to that of earth and there is evidence that water exists on the moon as well [5]. As a result of these findings, the possibility arises for aluminum and water propellants to be produced on the lunar surface, thus decreasing the take-off weight and greatly increasing the effective specific impulse of a mission. For example, calculations by Linne and Meyer show that the effective specific impulse for a mission can be doubled compared to that of an all Earth propellants mission if half of the propellant production is done in situ [6].

In this paper we present recent results obtained with the ALICE propellant and derivative mixtures. First, ground test motor pressure and thrust data are evaluated against an internal ballistic model taking into account mass flow contributions from the igniter, combustion efficiencies, and specific impulse efficiencies. Second, we compare the trajectory simulation results for the flight of a sounding rocket with the data recorded by the on-board data acquisition system and derive approximate performance data for the flight. Third, we report initial results with micron-sized aluminum, hydrogen peroxide, and water mixtures.

II. Internal Ballistic Model

A. Code Description

A lumped-parameter model was developed following the derivation by Heister [7] to determine the internal ballistics analysis of the combusting ALICE motor grains. The control volume considered in this model takes into account the geometry of the grains tested at the propulsion laboratory. While a simple approach, the assumptions inherent to a lumped-parameter model are quite appropriate in the present application as the grains tested had low aspect ratios L/D ranging from 1.2 for the 3.5” long grains to 2.3 for the 7” long grains and, therefore, the pressure variations along the chamber length can be neglected [7]. The assumed ALICE propellant formulation had an equivalence ratio of 0.75 and a characteristic velocity of 1333 m/s, based on CEA results [8]. Further, based on previous experimental results reported in the literature [9], a specific impulse of 210 s is assumed for the thrust calculations. Table 1 provides all the relevant input data for the following models.

Table 1. ALICE propellant properties used in the model.

Property	Value
Isp	210 s
c^*	1333 m/s
γ	1.13
Burning Rate Coefficients	
a	0.57
n	0.70

The purpose of the code is to predict the peak chamber pressure and thrust produced by the ALICE grains and to indicate the history of both parameters based on the measured strand burning rate and the calculated geometry of the grain. While propellant and motor parameters are adjusted in the model, detailed accounting of potentially important two-phase flow losses or nozzle flow losses is not within the scope of the present study.

The results presented below include that of two variants of the model. The first model variant is described in details by Wood *et al.* [10]. In this variant, the ALICE propellant properties are assumed as nominal and the pressure and thrust contributions of the igniter are neglected in developing the profile traces. It is used to predict the maximum thrust and chamber pressure prior to experimental testing of a new grain or chamber geometry. In the second variant, the pressure and thrust contributions of the igniter are added to the performance of the ALICE motor. One of the goals of this model is to determine the burnout time of the igniter. The operating pressure of the ALICE chamber is larger than the nominal pressure of the igniter, so the igniter propellant has a shorter total burn time. The modeling equations are adjusted to account for two different propellants burning at the same time and

chambers chocking and unchocking at different times. Following an experimental timeline, the igniter burns by itself first while the gaseous products pressurize the main chamber. During this time, only the igniter nozzle is choked. After some time, the ALICE propellant is ignited and begins to burn. Soon after ignition of the ALICE grain, the increase in pressure in the combustion chamber chokes the main nozzle and unchokes the igniter nozzle.
The conservation of mass equation, accounting for the individual burning rates of the ALICE and igniter propellants, is provided by Eq. 1.

$$\dot{m}_{in} - \dot{m}_{out} = 0 = \left((r_b \rho_p A_b)_{Igniter} + (r_b \rho_p A_b)_{ALICE}\right) - P_c \frac{A_t}{c^*_{mix}} \tag{1}$$

The expression c^*_{mix} is equal to a weighted average of the respective values for c^* based on the amount of mass contribution of each propellant during that time step. Since the igniter has four individual grains that are placed together, the number of segments is also taken into account in determining the burning area as given by,

$$A_b = 2\pi R_i L + (\#\text{ of Un} - \text{inhibited Sides})(\#\text{ of Segments})\left(\frac{\pi}{4}(2R_o)^2 - \frac{\pi}{4}(2R_i)^2\right), \tag{2}$$

Substituting the respective burning rate equations and rearranging the terms, Eq. 1 becomes,

$$\left((aP_c^n \rho_p A_b)_{Igniter} + (aP_c^n \rho_p A_b)_{ALICE}\right) = P_c \frac{A_t}{c^*_{mix}}. \tag{3}$$

Equation 3 cannot be solved directly for P_c. Instead, an iterative approach is taken to determine the value for chamber pressure, by matching the values of the inlet and outlet mass flow rates.

B. Output of the Model

The second variant of the prediction code accounts for the performance contributions of the igniter. The igniter geometric parameters are measured with a digital caliper (nozzle dimensions, grain size, etc.) and thrust data is available online [11]. Values for c^* and γ are estimated using typical AP composite values, determined from CEA [8]. Ballistic parameters were obtained from AeroTech and input into the code. However, the burning rate coefficients used did not yield pressure profiles that matched the data obtained from ThrustCurve.org [11]. Therefore, the ballistic parameters of the igniter were adjusted in order to match the ThrustCurve.org pressure profile.

The estimated chamber pressure is backed out using the thrust data, and values for the ballistic parameters are iterated upon until it agrees with the data. Figure 1 shows the agreement between the igniter data found online and the lumped parameter model, as well as a pressure profile using the AeroTech burning rate coefficients. The igniter data shown here corresponds to that of an Aerotech H180 commercial motor as selected for all tests of 7” long ALICE grains.

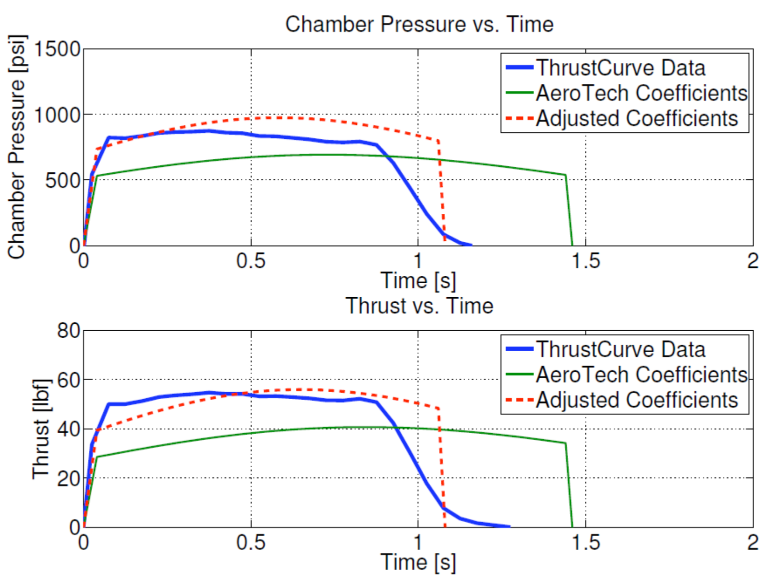

Figure 1. Lumped parameter model for the Aerotech H180 igniter compared to online thrust data and AeroTech coefficients

Based on the data from the static test fires, it is estimated that the igniter is burning by itself for approximately 0.45 seconds before the ALICE motor ignites. With this empirical data point, the chamber pressure and thrust profiles calculated with both variants of the model can be plotted on a common graph as shown on Figure 2.

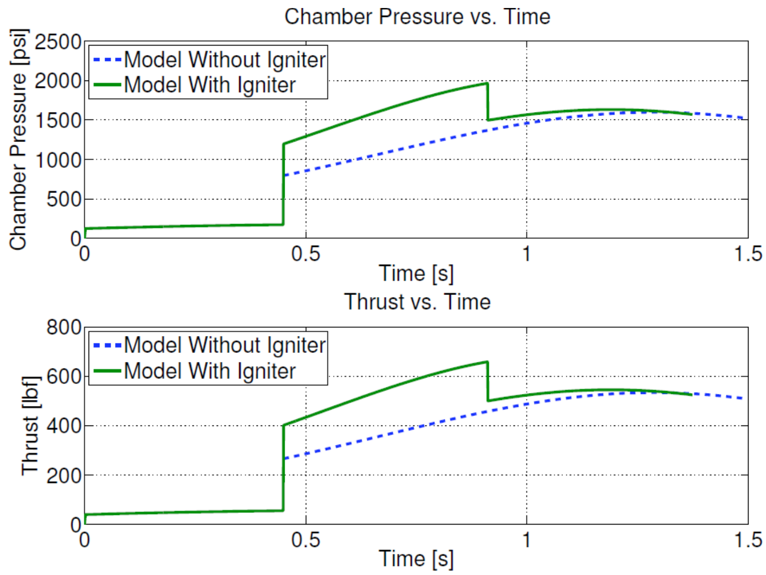

Figure 2. Calculated chamber pressure and thrust for 7" long ALICE grain

C. Model Calibration

To increase the accuracy of the second model, two different conditions are employed after the static test is complete. Post-test analysis shows aluminum oxide agglomeration on the throat of the nozzle. The thickness of the agglomeration is measured and assumed to grow linearly with time. This throat deposit is input into the code. Secondly, a performance efficiency is added to the ballistic parameters; a c^* efficiency to the pressure trace, and an *Isp* efficiency to the thrust. This is applied by estimating the average c^* efficiency for the entire pressure rise. A linear efficiency is applied, using the time at the beginning of the ALICE burn and the time at the peak performance values and the average c^* to determine the slope. A different set of efficiencies are used for the pressure fall in order to better match the experimental data. These parameters are adjusted until the model agreed with the experimental results. A similar approach is taken to determine an *Isp* efficiency. Figure 3 shows two adjusted models for the 7" grains; one with a throat deposit included, and one without.

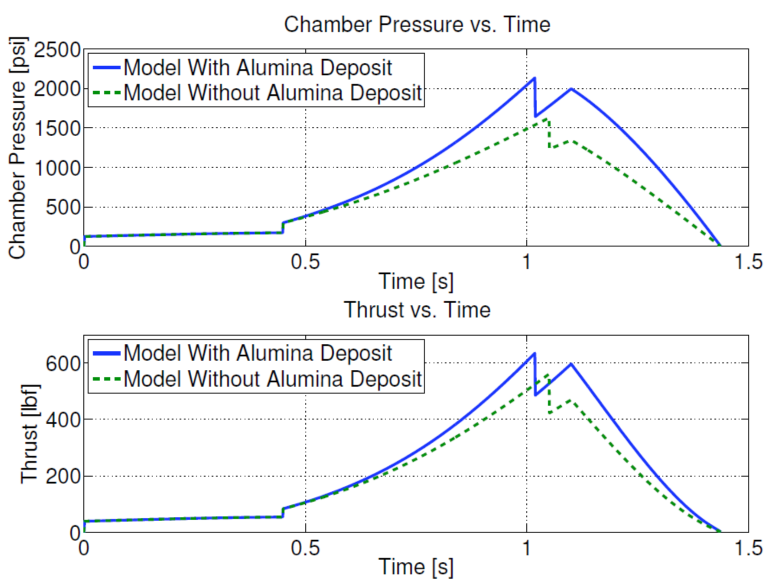

Figure 3. Comparison of models with and without alumina deposit

III. Aluminum-Ice Sounding Rocket

A. Ground Testing

Horizontal Configuration

The first test of the flight-weight motor followed five successful tests with a heavy-wall combustion chamber designed for three inch diameter grains of increasing lengths (3, 5, and 7”) [10]. Referred to as “Resodyn-6”, the test was in the horizontal configuration. A nozzle throat of 0.52” was selected to provide a predicted chamber pressure of ~1500 psi. The first test used a grain length of 6.75”, due to limitations of the grain-casting tool. A modification of the tool has been completed since the casting of the first grain to allow longer grains to be cast. The experimental results obtained with the first flight-weight grain are presented and compared with the modeling results in Figure 4. The test results show an average peak pressure around 1500 psi and a peak thrust of ~500 lb_f. The applied efficiencies are shown in Table 2.

Table 2. Applied efficiencies for computational model of Resodyn-6 test.

Property	Value
Start Time	0.4 s
Peak Time	1.05 s
End Time	1.4 s
Average Rise c* Efficiency	45%
Peak c* Efficiency	65%
Average Fall c* Efficiency	35%
Average Rise *Isp* Efficiency	65%
Peak *Isp* Efficiency	95%
Average Fall *Isp* Efficiency	60%

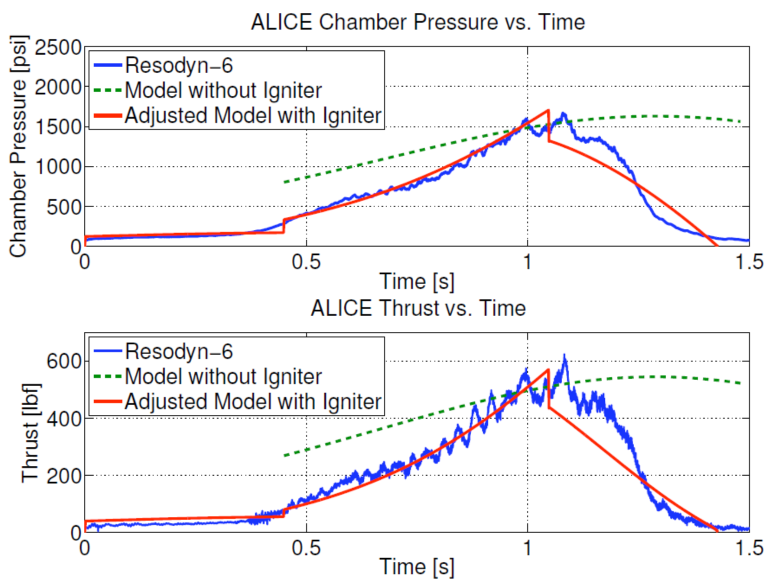

Figure 4. Comparison of 6.75” long ALICE motor test with lumped parameter models in the horizontal configuration

Vertical Configuration

A vertical static fire tests was conducted with flight-weight hardware prior to launch with an ALICE motor. Since all previous tests were performed horizontally, knowledge of how the grain and alumina slag behaved with the effects of gravity was not known. These concerns ranged from questions on whether the grain would become dislodged from the walls of the phenolic tube and slide toward the nozzle, or if the alumina slag would clog the nozzle. This vertical test was conducted using the same Aerotech H180 igniter as in prior tests. The grain was slightly longer, from 6.75” to 7”, compared to the previous horizontal test but with a nearly identical packing density (within 2.2%). Figure 5 d*Isp*lays the experimental data of the vertical test and the predictions obtained with the performance prediction model and Table 3 d*Isp*lays the efficiencies applied to the computational model in order to match the vertical flight-weight experimental data.

Table 3. Applied efficiencies for computational model of Resodyn-7 Test.

Property	Value
Start Time	0.4 s
Peak Time	1.1 s
End Time	1.4 s
Average Rise c^* Efficiency	50%
Peak c^* Efficiency	75%
Average Fall c^* Efficiency	35%
Average Rise *Isp* Efficiency	70%
Peak *Isp* Efficiency	100%
Average Fall *Isp* Efficiency	60%

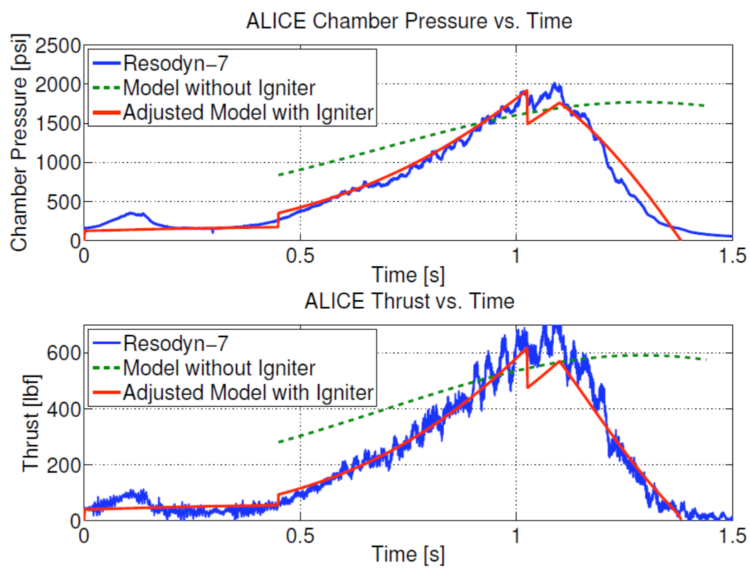

Figure 5. Comparison of 7" long ALICE motor test with lumped parameter model in vertical configuration

It is encouraging that the lumped parameter models capture the experimental peak values of pressure and thrust for both the 5" and 7" grains. Despite the simplifying assumptions in the model, capturing these performance metrics provides an indication of an attainable *Isp* of ~214 s and a c^* of ~1330 m/s. Table 4 shows the average rise and peak efficiencies used in order to match the pressure and thrust profiles obtained with the flight weight motor tests. Improved propellant formulations with higher equivalence ratio (closer to stoichiometric) and appropriate additives should increase the experimental specific impulse to values well above 200 s.

Table 4. Applied Efficiencies to Match Experimental Data

Test	Average c^*	Peak c^*	Average *Isp*	Peak *Isp*
Resodyn – 6	45%	65%	65%	95%
Resodyn – 7	50%	75%	70%	100%

B. ALICE Launch

The demonstration flight of the ALICE propellant with an unguided experimental rocket was a proof of concept for more advanced rockets using similar nano-energetic material based propellants. The flight followed a rigorous design process and extensive ground testing of the ALICE rocket motor thus minimizing the likelihood of ignition issues or motor structural failure.

The experimental rocket chosen for the flight is an all-carbon-fiber, minimum diameter, 98 mm high power rocketry kit known as a Mongoose 98. Two launches were performed with this rocket; the first flight used a K-780 commercially available rocket motor to test the avionics bay and deployment of the parachutes and the second used the flight-weight motor casing with an ALICE propellant grain. All launch operations were carried out at a remote area located approximately 12 miles south-west of West Lafayette. Known as Scholer Farm, this land is owned by Purdue and managed by the Animal Sciences Research and Education Center (ASREC). The first flight, with the K780 commercial motor, took place on June 14th, 2009. This flight is described in details by Wood et al. [10] along with a description of the flight weight motor casing design and implementation in the Mongoose 98. The demonstration flight of the ALICE propellant took place approximately two months later on August 7th, 2009.

For both test flights, we used a commercial ballistic trajectory simulation code (Rocsim-PRO) to calculate flight-vehicle performance (altitude, range, velocity, acceleration). This code simulates flight with the addition of wind speed and direction, atmospheric thermal gradients, pressure, location latitude/longitude, launch rail azimuth/elevation, and more. In addition it incorporates the NASA SPLASH code in order to perform 6-DOF Monte-Carlo simulations based on the uncertainty values in physical parameters such as mass properties (moment of inertia, center-of-gravity), aerodynamics (drag coefficient, center-of-pressure, fin cant angle), propulsion (total impulse, propellant mass, thrust axis), wind direction/velocity, and launch guide angle uncertainties.

Based on the thrust profile from the hot-fire test performed with the 7” long ALICE grain, as well as the new flight-weight motor design, the Rocsim-PRO simulations predicted that the 30 lb flight vehicle would depart the launch rail in 0.9 seconds, achieving a velocity of 67 ft/s at rail exit. The simulations also predicted a maximum acceleration of 16 G’s, maximum velocity of 187 mph (Mach 0.24), and a nominal altitude of 1,200 ft under no wind conditions.

Several constraints limited the achievable altitude with the current ALICE powered rocket. First, the combustion and flow losses observed during the last six static test firings lead to total impulse values of about 60% that of the predicted values. These losses are being addressed in on-going work with improved propellant formulations including additives and alternative formulations to achieve higher specific impulse and lower the alumina content of the products. Second, the flight-weight casing for the ALICE propellant had to sustain pressures up to 2000 psi requiring thicker walls, thus increasing vehicle weight compared to a traditional SRM. In addition, the energy required for igniting the current ALICE propellant formulation is significantly higher than that required for a standard solid propellant. This leads to added weight for an igniter casing and an interface with the ALICE casing capable of sustaining high pressures and designed in such a way that the combustion gases do not impact the aluminum walls. Weights were also added just below the nose cone to yield a higher stability margin. While designed for flight with safety factors around 1.5, the heavier casing reduced the maximum altitude achievable with the rocket. Finally, the burning rate of the current ALICE formulation is on the order of 1 inch per second at the nominal operating pressure of 1500 psi. This high burning rate means that a larger web thickness is required to sustain the ALICE combustion over sufficiently long durations. In turn, larger grains require heavier casings. The current design is a trade-off between the aforementioned constraints. Further improvements of the propellant formulation should address these constraints, thus reducing the weight of the flight-weight casing in an effort to achieve better flight performance.

The ALICE demonstration flight took place of a fairly cool (~70°F ambient temperature) and calm (~2 mph wind at launch site) day. Figure 6 shows the ALICE vehicle on the stand ready for takeoff (left), soon after ignition (middle), and flying under ALICE soon after it cleared the launch tower (right).

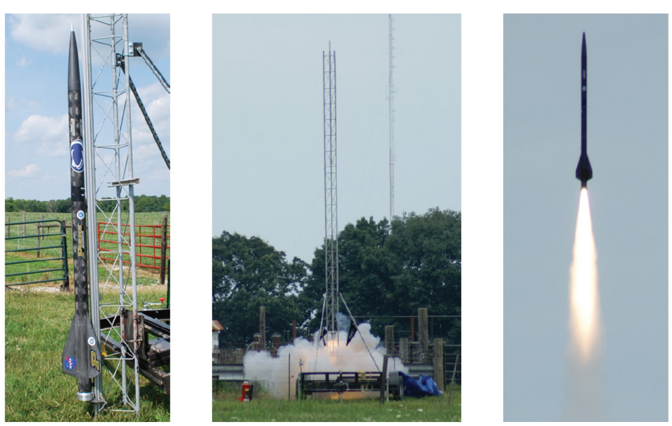

Figure 6. Images from the ALICE flight test: Rocket on launch platform (left), ignition of the ALICE propellant (middle), and rocket in flight (right)

The rocket coasted after the grain was depleted and reached a peak altitude of 1292 ft. This altitude is very close the estimate of 1200 ft obtained from Rocsim-PRO assuming no wind. The data recorded from the R-DAS is shown in Figure 7.

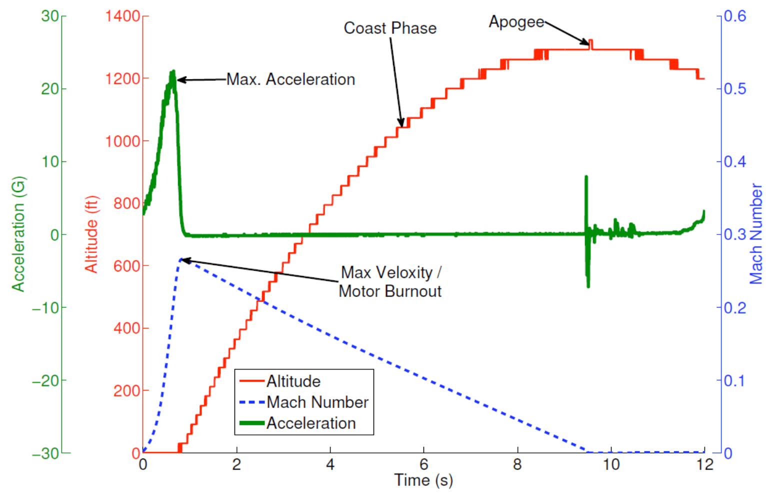

Figure 7. R-DAS Flight-data from test launch of the flight vehicle powered by the ALICE motor

This close agreement between recorded flight data and predictions indicates that the thrust profile and thrust magnitude experienced during flight were very similar to those recorded on the ground with the flight hardware. Similarly, it is observed that the peak *Isp* of 210 s calculated from the ground test data is a good estimate for the flight *Isp*.

IV. On-Going Research

This work has shown that a "green" propellant made exclusively from aluminum and water is possible. Aluminum and ice propellants can serve as a stepping stone to the development of similar, high-performance formulations such as aluminum + hydrogen peroxide and aluminum hydride + hydrogen peroxide. The theoretical *Isp* performance of these propellants as compared to several ALICE varieties is shown in Table 5 and Figure 8. Assuming larger aluminum particles could be used, the amount of aluminum oxide present in the aluminum particles would be reduced to less than 1%, boosting the theoretical performance of the mixtures. As shown in Table 5, mixtures containing peroxide as the oxidizer exhibit much higher flame temperatures than both aluminum-water and alane-water. This should result in improved combustion efficiency and *Isp* values for mixtures containing hydrogen peroxide.

Table 5. Calculated results for Pc = 1000 psia, and *Isp* optimized for expansion to 14.7 psia and *Isp* vac uses an expansion ratio of 40

	Al - H_2O	Al - H_2O_2	AlH_3 - H_2O	AlH_3 - H_2O_2	AP/Al/HTPB[#]
Peak Isp (s) (Pe = 14.7 psia)	232.8	258.7	279.6	314.7	249.8
Peak Isp vac (s) (ER=40)	284.7	313.1	332.4	379.7	293.2
Chamber Temperature (K)	3084	3901	2421	3730	2832
C* (ft/s)	4466	4979	5422	6082	5003
O/F	1.0	2.5	0.9	0.9	3.8
Equivalence Ratio	1.00	0.75	1.00	3.85	-

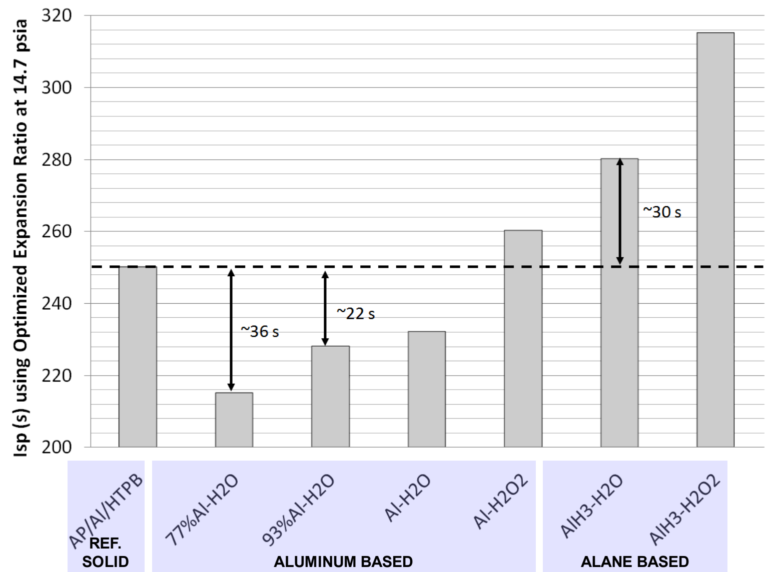

Figure 8. Optimal *Isp* expanded to 14.7 psia from a chamber pressure of 1000 psia for aluminum-water, aluminum-hydrogen peroxide (100%), alane-water, and alane-hydrogen peroxide (100%). Peak *Isp* values compared with the value of 249.8 s obtained from a solid propellant formulation AP/Al/HTPB/Fe_2O_3, with the respective ratios of 70.1/10.9/18/1 using the same code and conditions [8]

Motivated by the increase in theoretical performance and the higher temperatures, testing has begun to characterize the burning rate of mixtures containing micron aluminum, 4.5% fumed silica by mass, and hydrogen peroxide. The fumed silica is added to the mixtures to help with gelling. Images of 30% hydrogen peroxide ALICE quartz tubes burned in the constant volume combustion bomb are shown in Figure 9. Initial strand burning experiments using low concentrations of hydrogen peroxide suggest that the higher flame temperatures have the potential to improve motor combustion efficiency and could reduce the formation of solidified aluminum/aluminum oxide inside the combustion chamber. Strands that have been burned containing 60% hydrogen peroxide show very little post combustion deposits at all.

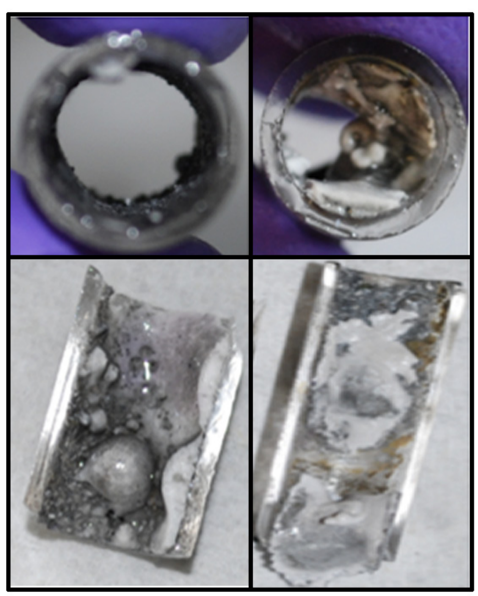

Figure 9. Comparison of the combustion products of both 30% peroxide containing ALICE using H2 (3 µm) aluminum (left) and ALICE containing 80 nm aluminum and water (right).

Preliminary burning rate data shown in Figure 10 shows that burning rates with hydrogen peroxide + water and micron scale aluminum lie above and below of the burning rate of ALICE depending on particle size and hydrogen peroxide concentration. Increasing the aluminum particle size appears to have a dramatic effect on the burning rate for aluminum sizes below H10. For sizes larger than H10, there appears to be less of an effect. This behavior suggests that for these particle sizes and propellant compositions, there is a transition between diffusionally limited and kinetically limited combustion. Mixtures containing the largest aluminum tested (H10 and H15) with only 30% hydrogen peroxide exhibit less stable burning, suggesting a lower deflagration limit for those mixtures. Safety testing is concurrently being done prior to conducting burning rates. The eventual goal of these exercises is to converge upon a high performance formulation containing 90%+ hydrogen peroxide.

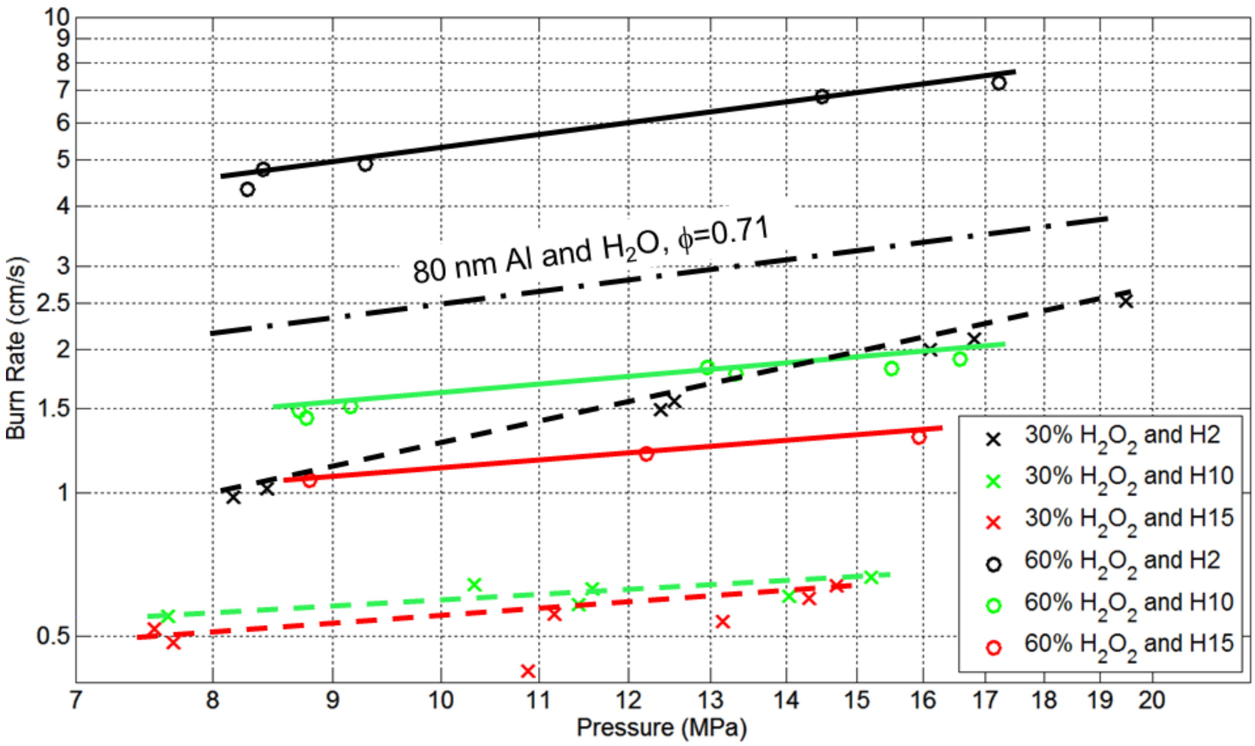

Figure 10. Burning rate data for hydrogen peroxide containing ALICE mixtures burned at O/F = 1.1

V. Conclusion

The ALICE propellant has shown promise as a rocket propellant in static test firings and with the demonstration flight of a sounding rocket to 1,300 ft. However, much work remains to make it a viable propellant. The success of the test firings and of the launch relied in part in the accurate accounting of the ALICE grain internal ballistic using a versatile lumped-parameter model. With the simplest version of the model, basic propellant properties, grain geometries, and mass conservation equations lead to pressure and thrust predictions. The second version of the model includes the performance of the igniter in order to predict igniter burn out time and give a more accurate burning history. Additionally, both *c** and *Isp* efficiencies can be applied to this model providing a means to match experimental data.

The fuel-lean mixtures described in this paper are being improved with more stoichiometric mixtures or by replacing some of the water with hydrogen peroxide. Current combustion calculations and experiments on aluminum and hydrogen peroxide suggest promising improvements over ALICE in terms of specific impulse, burning rate, combustion efficiency, and reduced aluminum/aluminum oxide solid product accumulation. Future work may include a second launch of the sounding rocket with additional instrumentation on-board and an optimized propellant.

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