New Solid Propellant Additives: Evaluation for NASA Mission Use Cases

Timothy P. Kibbey[1]
NASA George C. Marshall Space Flight Center, Huntsville, AL, 35812, USA

Researchers and small companies have been investigating and developing new solid rocket motor propellant ingredients with renewed vigor. Lithium-aluminum alloy is an ingredient of particular interest, but most of the advertisement about its benefits are focused on defense tactical rocket applications. This paper develops a framework to evaluate this and other propellants against standard aluminized composite propellant for mass-limited missions like many NASA in-space applications. It shows a way to estimate density's effect with an exponent less than 1 depending on mission and technology parameters, and an algorithm for directly calculating delta-velocity or payload performance improvement.

I. Nomenclature

Al	= aluminum
AP	= ammonium perchlorate
ΔV	= change in velocity
f_p	= performance factor
g_c	= 9.80665 m/s^2
HTPB	= hydroxy-terminated polybutadiene
Isp	= Specific Impulse
Li	= lithium
m	= mass
ρ	= propellant bulk density
SRM	= Solid Rocket Motor

subscripts:

i	= inert
pay	= payload
ref	= reference
0	= initial

II. Introduction

NASA in-space missions have a long history of utilizing solid rocket motors, and future missions could benefit from their continued inclusion. New propellant ingredients and concepts will be examined here for their applicability to these NASA missions.

Escape stages, de-orbit stages, lunar and planetary surface launch stages, gravity well or apogee kick stages all tend to require mass-limited optimization for either change in velocity (ΔV) or maximum payload. This contrasts with the metrics often reported for new propellant combos that are often more

[1] Motor Performance SME, Solid Propulsion and Pyro Devices Branch, and AIAA Member.
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tailored to volume-limited tactical missile application, and that focus on range. This paper develops a performance framework for mass-limited missions and examines recent proposed propellant chemistries. This involves these steps:

- Define a combination space over ingredient ranges, and compute bulk density
- Perform Chemical Equilibrium Analysis (CEA) set at constant expansion ratio, rather than expanded to one atmosphere, and examine vacuum Specific Impulse (Isp)
- Evaluate the rocket equation for maximum ΔV at fixed payload and initial mass, and approximate performance factor as density$^{m}\cdot$Isp and identify the exponent *m*
- Evaluate the rocket equation for maximum payload at fixed ΔV and initial mass
- Identify where mission design (ΔV requirement) and SRM architecture (f_i) drive optimum propellant formulation for a given propellant ingredients set
- After this ideal analysis, identify what non-idealities may push the performance increase beyond that indicated by the theoretical work and estimate the maximum performance increase attainable by the candidate propellant technology

Additional non-idealities to consider:

- How different propellants may differently affect combustion-and-expansion efficiency
- How different propellants may differently erode nozzle and insulation components
- Economic and environmental aspects of propellants and processes

III. Explicit Useful Variables in the Ideal Rocket Equation

The ideal rocket equation is classically written in Equation (1), with two mass variables.

$$(1)\quad \Delta V = -g_c Isp \ln\left(\frac{m_{final}}{m_{initial}}\right)$$

Throughout, g_c is the "gravitational constant," merely the units conversion 9.80665 m/s^2 so that *Isp* can be expressed in the familiar "seconds." The mass variables may be rearranged strategically as in Equation (2).

$$(2)\quad \Delta V = -g_c Isp \ln\left(1 - \frac{1-\frac{m_{pay}}{m_0}}{1+f_i}\right)$$

Now it is written in terms of two independent mass-related choices: Here the payload ratio $\frac{m_{pay}}{m_0}$ represents the mission choice, and the inert mass fraction, $f_i = m_{inert}/m_{prop}$, represents the SRM technology choice. For example, a motor like the STAR-48BV[i] would have a low inert mass fraction, while a small boost-sustain motor as designed for Mars surface launch would have a higher inert mass fraction; this coarse-tuning mass fraction choice is independent of the propellant ingredients being traded.

It remains to show how propellant choice affects the inert mass fraction, an important fine-tuning step, and the only way that propellant density factors in (Eq. 3):

$$(3)\quad \Delta V = -g_c Isp \ln\left(1 - \frac{1-\frac{m_{pay}}{m_0}}{1+f_{i,ref}\frac{\rho_{ref}}{\rho}}\right)$$

This models SRM inert mass as fundamentally a motor volume factor, such that a higher density propellant has a proportionally lower inert mass fraction compared to the same design type with a reference propellant.

In summary, Equation (3) shows two independent stage architecture parameters (inert mass fraction for SRM technology and either payload mass ratio or ΔV for mission), and two propellant parameters (Isp and density). A typical comparison between propellants shows relative Isp, and/or relative density*Isp. However, Equation (3) links density and specific impulse more rigorously, for the mass-limited mission assumption (payload and initial mass constant). For comparison to previous work, and for handy quick estimates, it is convenient to estimate this linkage with a density exponent as in Equation (4)[ii], which will necessarily depend on the mission and SRM technology choices.

$$(4)\ f_p = \frac{\Delta V}{\Delta V_{ref}} = \frac{\rho^m}{\rho_{ref}^m}\frac{Isp}{Isp_{ref}}$$

The value of the exponent *m* can be approximated both analytically – understanding that to first order, the exponent is the same as the linear slope around (1,1) – and numerically – by fitting Equations (3) and (4) over a small range of density ratio. The results of both methods are shown in Figure 1. The author is not sure why the two approximations diverge at larger $f_{i,ref}$, but the following conclusions can be drawn:

- In all cases, the density exponent is less than 1/3, suggesting that "rho*Isp" is a significant overstatement of density's importance on mass-limited missions
- Density is more important on lower payload (higher ΔV) and higher inert mass fraction stages

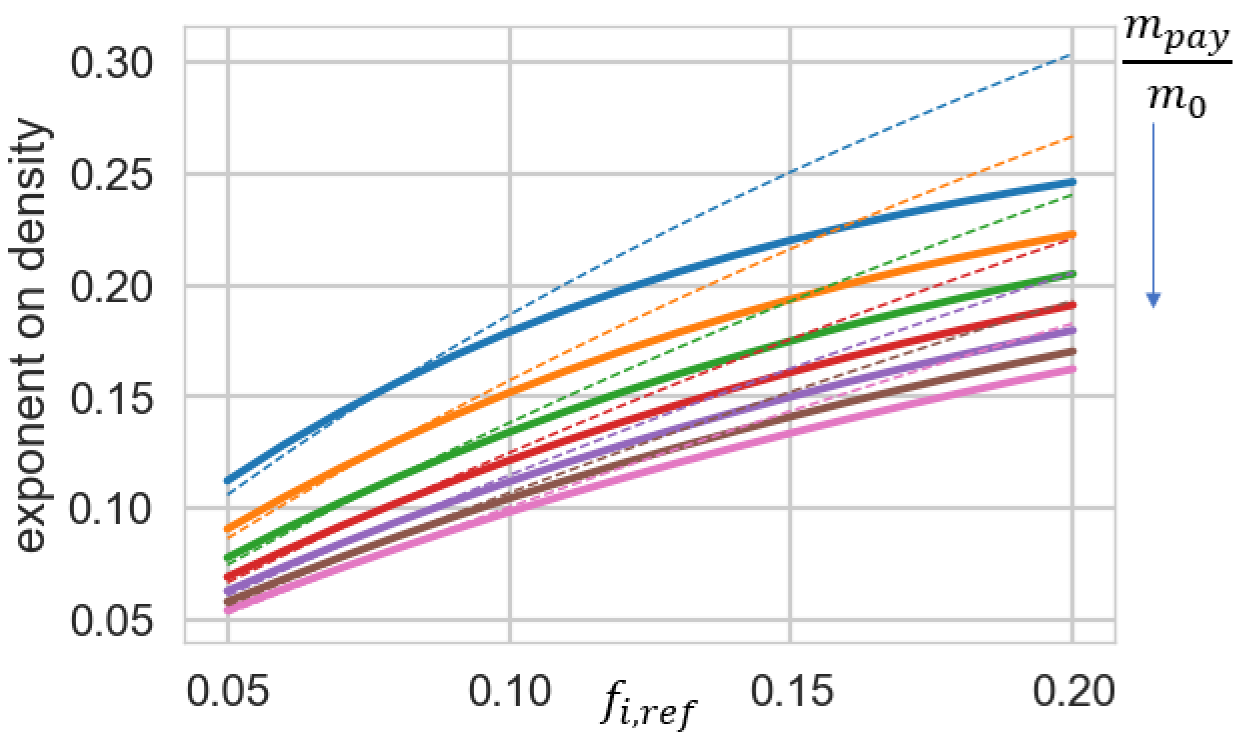

*Figure 1: **Numerical** and Analytical (- - -) Approximations of Density Exponent over payload ratio of 0.2 to 0.8*

Note that these observations relate to propellant choices within a stage architecture, and are not expected to adequately compare diverse stages, e.g., a solid rocket to a liquid rocket stage[iii]. Recommended use is to choose some range of the density exponents to make a ballpark estimate to compare among solid propellants, and then use Equation (3) for optimizing the propellant and for estimating performance increase versus a reference.

The above analysis is useful for identifying where a propellant can be customized for optimum performance by maximizing ΔV. Maximizing ΔV is useful in some NASA missions – sometimes 5-10% more ΔV allows for more launch opportunities, adding flexibility to mission timelines. In other missions, the desire is to maximize payload for a fixed ΔV and stage initial mass. The optimal propellant composition within a propellant family will be the same whether maximizing ΔV or payload. But the way the mission and SRM technology impact the comparison to a reference propellant may be a bit different.

IV. Reference Propellant: Aluminum, AP, HTPB

Propellants composed of aluminum (Al), ammonium perchlorate (AP), and hydroxy-terminated polybutadiene (HTPB) are the reference family for this study. Ranges of the ratios of the 3 components were evaluated with NASA's Chemical Equilibrium Analysis (CEA) program.

The first independent variable is polymer volume ratio. Different volume ratios reflect different propellant strength and strain capability to first order, so while changing other variables, polymer volume assures that propellants are compared at like mechanical behavior. For this study, an expansion ratio of 54.8 was chosen to match the STAR-48B(V) reference motor, used on hundreds of orbit insertion and space probe missions. Table 1: STAR-48BV Reference Information shows additional STAR-48BV reference information that will help judge these results.

Table 1: STAR-48BV Reference Information

Expansion Ratio	54.8
Isp, propellant, s	294.2
Isp, effective, s	292.1
Inert mass fraction f_i	0.0783
Aluminum mass fraction[iv]	18%
Polymer volume fraction	22%
Theoretical Bulk Density, g/cm^3	1.813

The orthogonal axes chosen were 10%-28% polymer volume fraction and 70%-90% AP/(AP + Al). The resulting density range versus aluminum mass fraction is shown in Figure 2, covering a greater than 15% range in density.

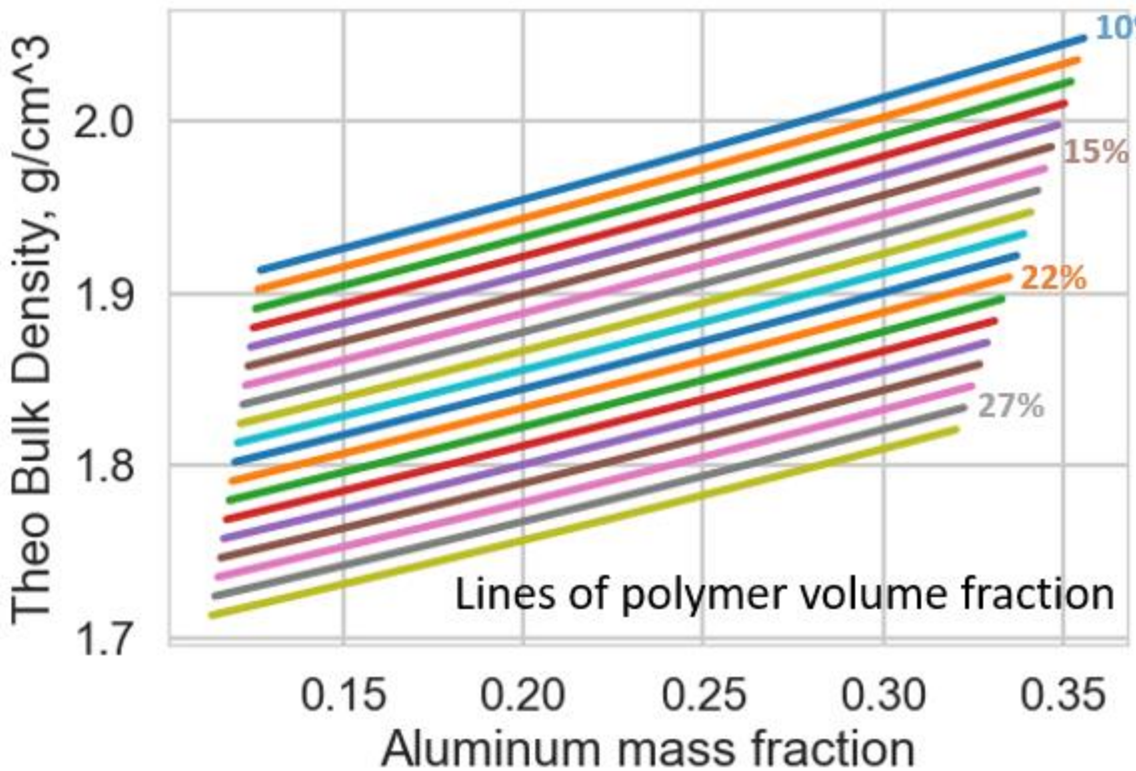

Figure 2: Theoretical Density of the Al/AP/HTPB Evaluation Space

Figure 3 shows theoretical vacuum Isp itself. The full range as described above is sufficient to bound maximum Isp with no restriction on polymer volume fraction. Next, note that the STAR48BV reference point is positioned at the maximum Isp for its amount of aluminum: given 18% aluminum, the polymer volume ratio is optimal. However, the data suggests that even with limiting to this volume ratio for mechanical properties purposes, formulations with a few more percentage points of aluminum would further increase theoretical Isp. However the designers of this venerable propellant have seen fit to hold it at 18%. This is perhaps where efficiency considerations come into play: The as-designed STAR48BV combustion-and-expansion efficiency is 91.4%, computed by comparing the catalog value to the CEA computation at STAR48BV's propellant, expansion ratio and average pressure. If moving aluminum content from 18% to 22% increases theoretical Isp by a mere half a percent but risks additional two-phase-flow losses that could be greater, then it is not worth it. This is one of the problems new-propellant researchers are seeking to address. Finally, even if a technology advancement allows for a higher volume-loaded propellant, it is only worth 1% Isp or less.

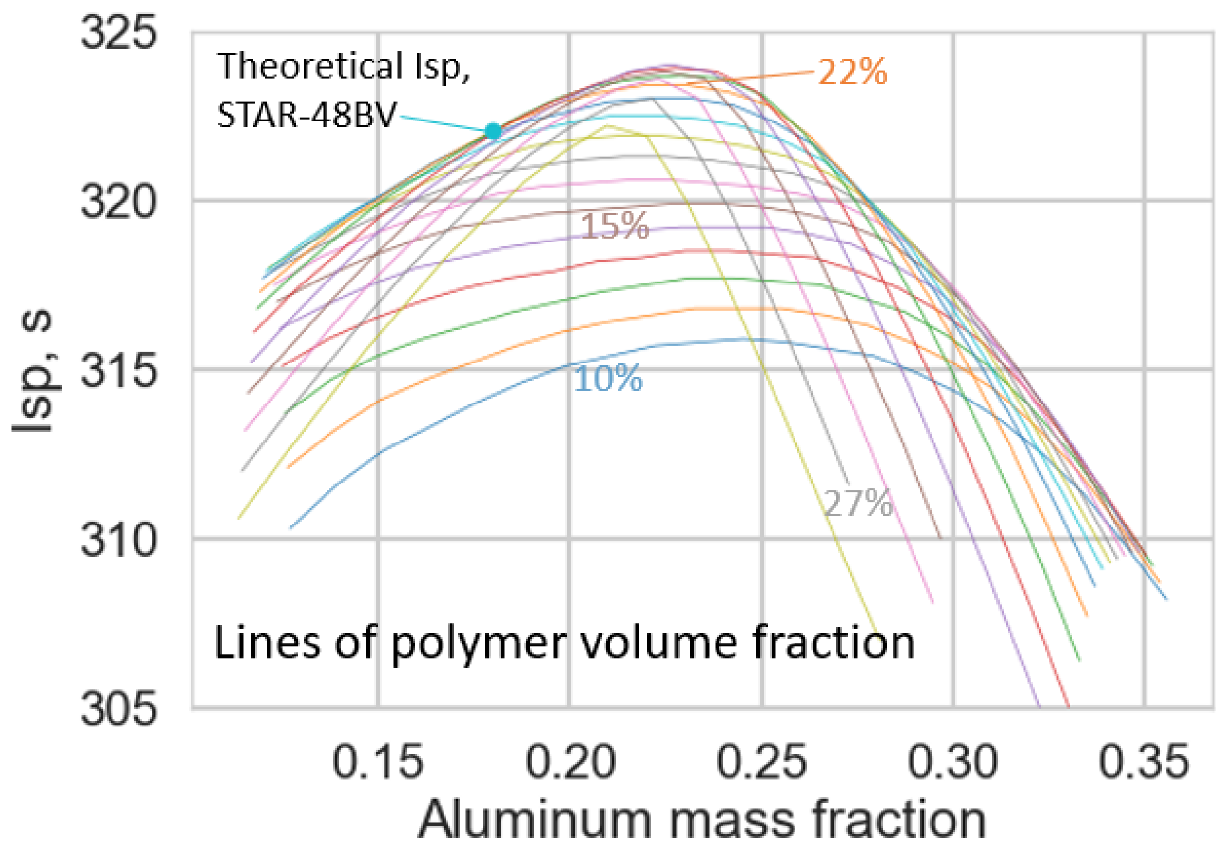

Figure 3: Theoretical Vacuum Isp, Al/AP/HTPB

Now for the density aspect. Figure 4 starts with density times Isp, as this is a long-considered figure of merit, though the preceding analysis suggested a lower weighting on density is appropriate for in-space mass-limited missions. Unsurprisingly, the peak $\rho \cdot Isp$ requires ever-reducing polymer volume fraction. As discussed above, for the present study, density's impact is at an exponent of 0.3 or less. The 0.3 exponent results are shown in Figure 5. In that case there are now more solutions potentially available above the reference performance, if the volume fraction and efficiency concerns could be overcome within the Al/AP/HTPB propellant family.

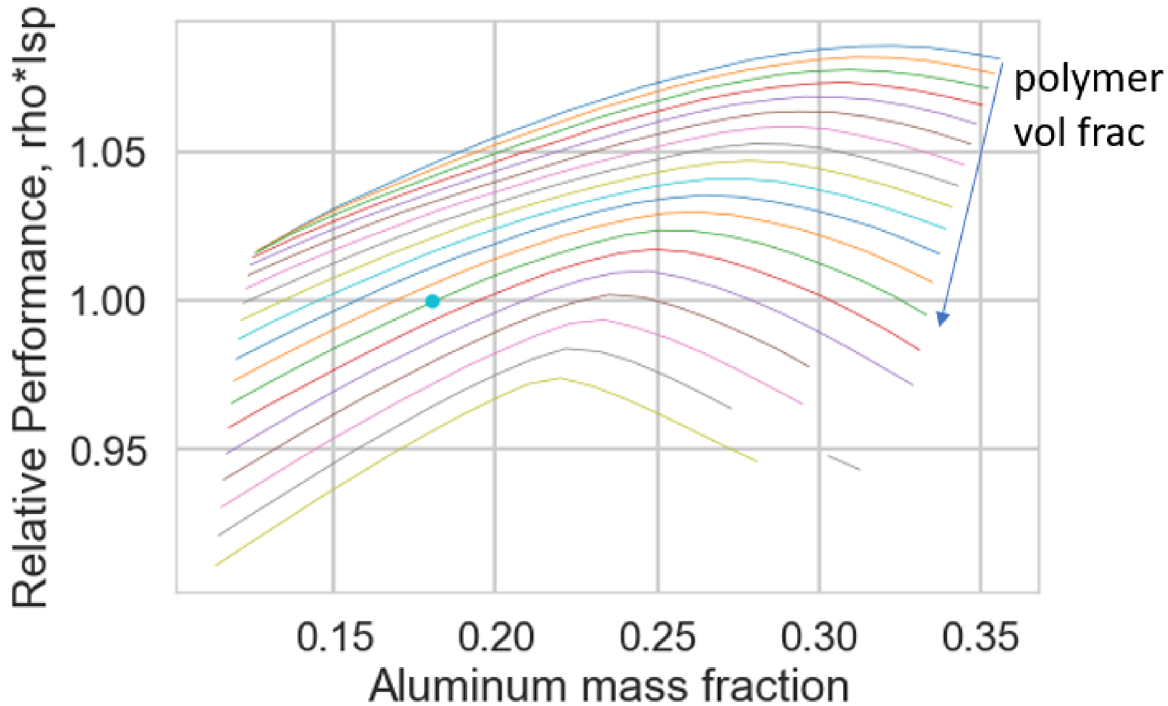

Figure 4: Propellant Performance Relative to STAR-48BV, density·Isp

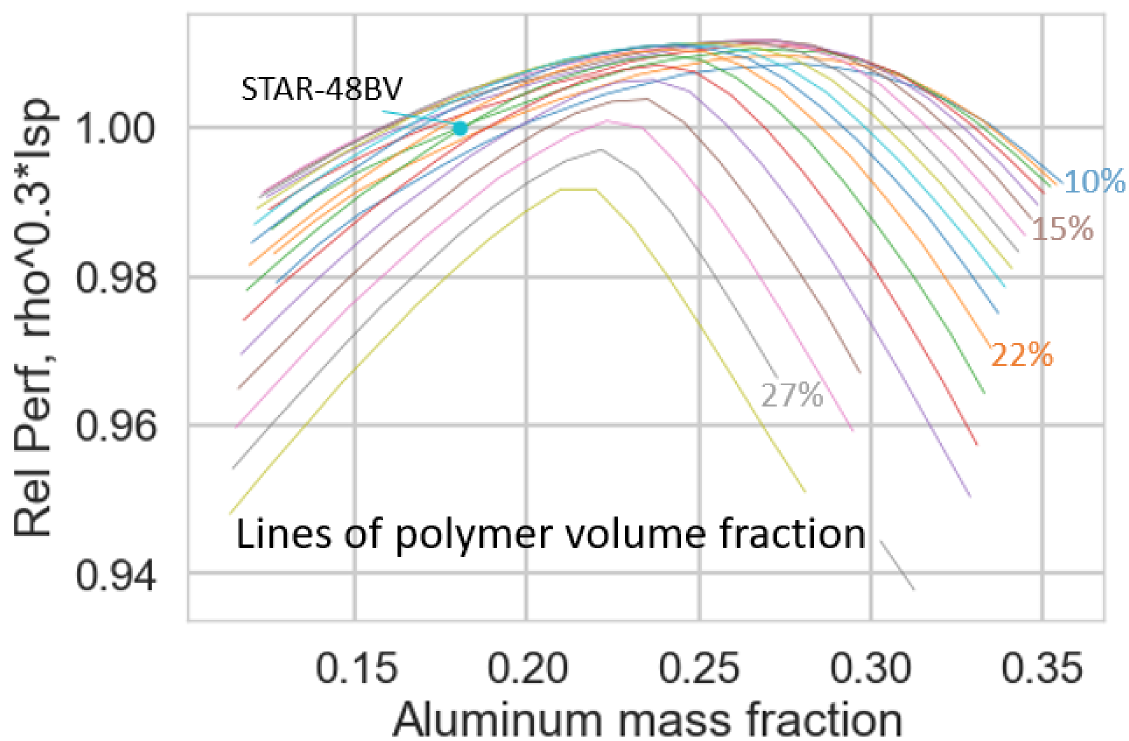

Figure 5: Propellant Performance Relative to STAR-48BV, density^0.3·Isp

V. Lithium-Aluminum propellants

Lithium-Aluminum propellants have been examined for their theoretical Isp improvement, for their reduction of large aluminum oxide particles that increase two-phase flow losses, and their reduction of hydrochloric acid in the exhaust[v]. The primary challenge is to encapsulate the high-Lithium alloy with an impermeable coating, so the lithium doesn't oxidize before it is intended to combust during motor operation.

The following set of parameters was used to describe a Lithium-Aluminum evaluation space. To compare only the effects of the different metallization, only the 22% polymer volume fraction commensurate with the reference STAR48BV was considered. Orthogonal axes were set at 60% to 90% AP-to-total-solids volume ratio and 4% to 60% lithium-to-total-metal volume ratio. This equates to a max lithium loading by mass of about 3:7 Li:Al at 22% aluminum. Figure 6 shows the lithium, aluminum and density space.

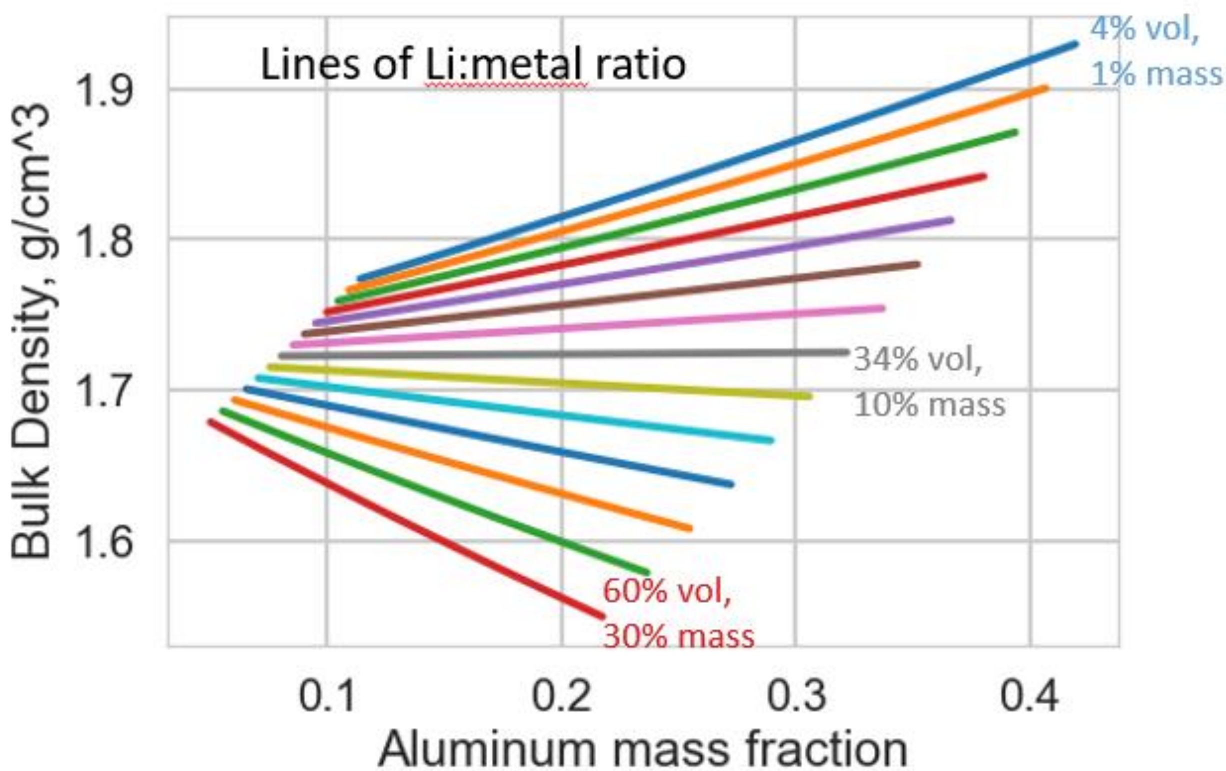

Figure 6: Evaluation Space for Lithium Aluminum propellants

The theoretical Isp results are shown in Figure 7. This achieves a maximum theoretical Isp gain of 10 sec over the reference SRM. Note, this all assumes that the CEA thermo database and inclusions is adequate for lithium-aluminum combustion.

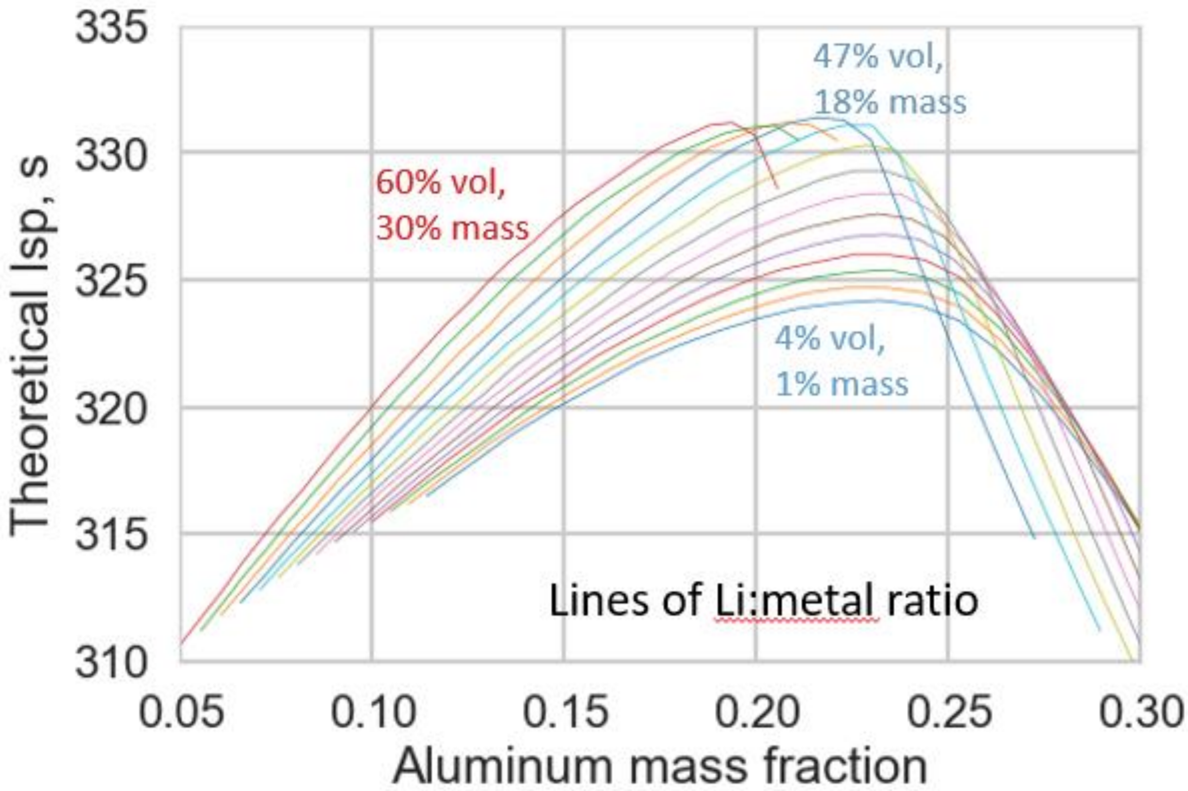

Figure 7: Theoretical Vacuum Isp, Li/Al/AP/HTPB propellant

Delta-V Performance of Lithium-Aluminum Propellants

Equation (3) was used to assess the performance and optimized formulation of Lithium-Aluminum propellant. For comparison to the real STAR48BV system and for realistic mission performance, an Isp efficiency has been applied to all subsequent results matching that of the STAR48BV. As discussed before, the optimal point depends on the mission parameter (either stage payload:gross mass or ΔV) and the SRM technology parameter (inert mass fraction). Figure 8 shows ΔV performance at an example condition of fixed payload-to-gross-mass-ratio of 0.3 and reference inert mass fraction of 0.0783. For comparison, the reference STAR48BV parameters result in a ΔV of 3002 m/s for this scenario. Thus the ΔV performance improvement if targeting the optimal Li/Al propellant formulation would be about 1.7%.

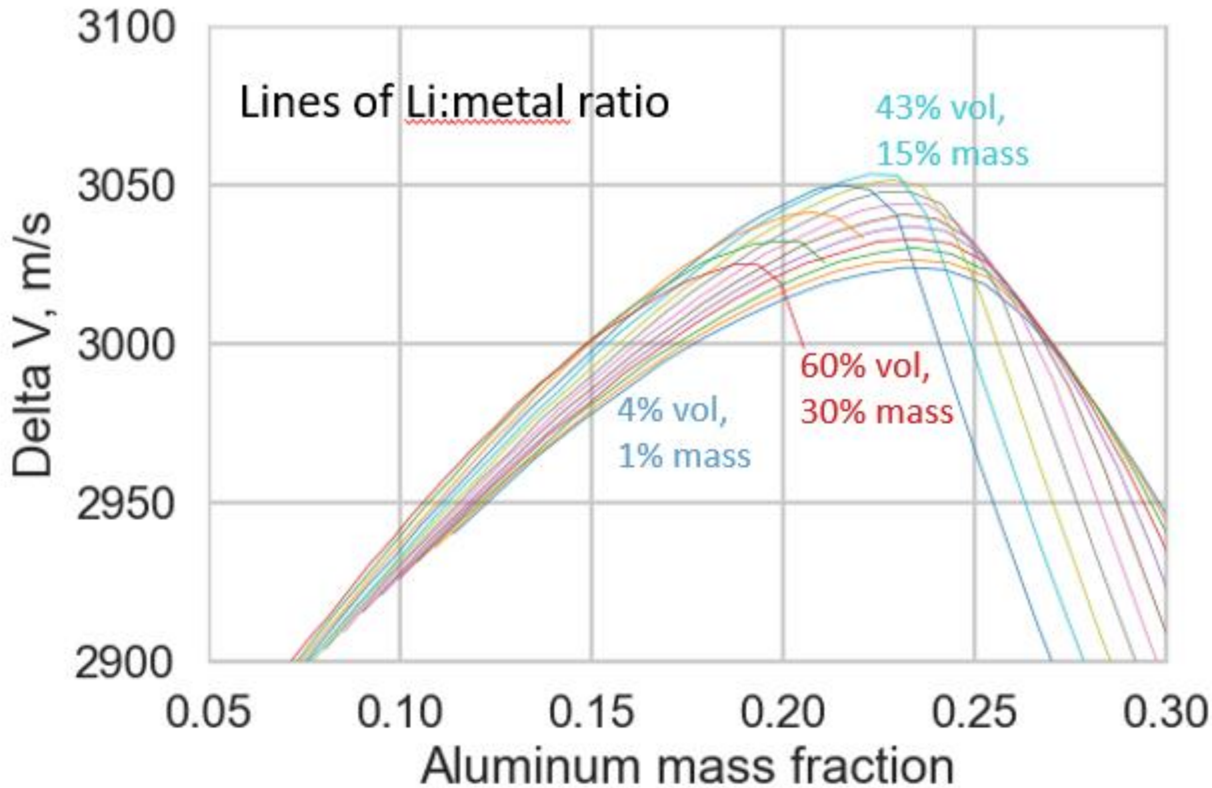

Figure 8: Example ?*V Performance: Li/Al/AP/HTPB at 0.3 payload mass fraction, 0.0783 inert mass fraction*

The illustration just completed can be done over the range of possible combinations of reference inert mass fraction and payload to initial mass ratio. An algorithm computed a dataset for each combination of payload mass ratio and inert mass fraction and selected the point of max performance. These maxima were compared to aluminized propellant maxima, and the results plotted in Figure 9.

For the case of maximizing ΔV at fixed payload and gross stage mass, the Lithium-Aluminum propellant can reap the highest benefits for SRM stages with high reference mass efficiency (low $f_{i,ref}$). For example, in these theoretical performance terms, it is more helpful to put this propellant into a STAR48BV-type motor than in a Mars Sample Return Ascent Vehicle stage. Furthermore, the “smaller” the mission (m_{pay}/m_0 closer to 1), the more effective switching propellants to the optimized Li/Al formulation can be, though this is weaker for small $f_{i,ref}$.

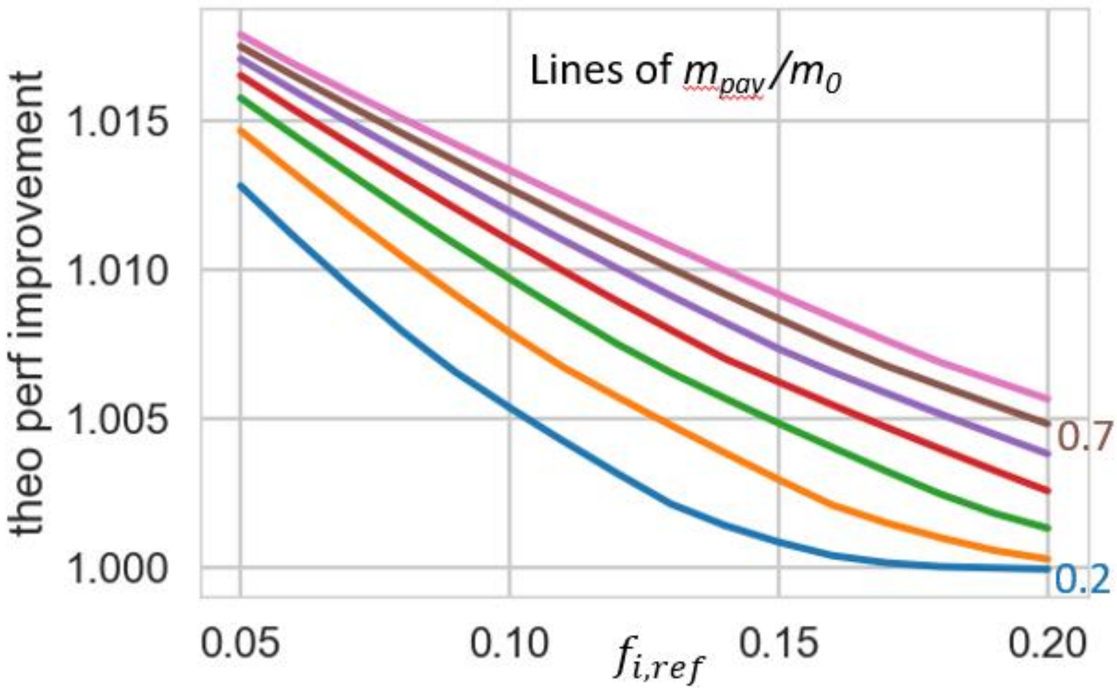

Figure 9: Li/Al ΔV performance improvement over mission/technology space

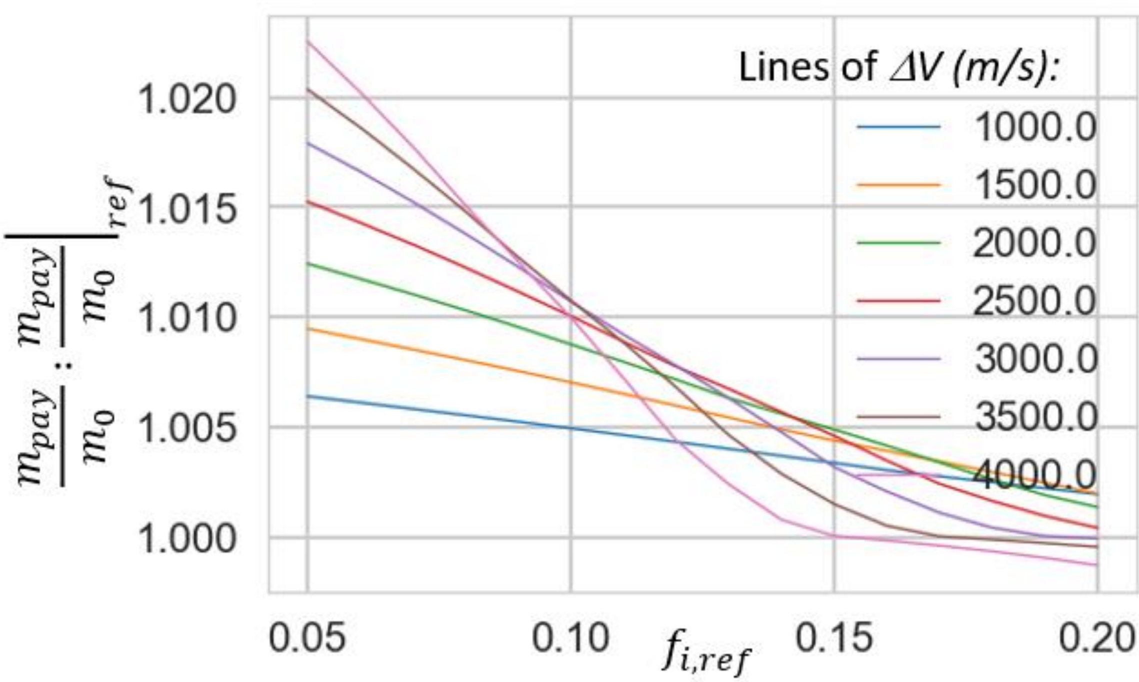

Figure 10: Li/Al Payload ratio performance improvement over mission/technology space

Payload Performance of Lithium-Aluminum Propellants

Equation (3) can be algebraically solved for m_{pay}/m_0. This is perhaps a more common mission usage: find the propulsion system that maximizes payload to a set ΔV requirement. The same maximization and comparison to aluminized propellant algorithm was performed, but over a range of ΔV and comparing the max payload ratio attained. **Error! Reference source not found.** shows the results for lithium-aluminum propellant compared to the aluminized propellant family. Note that for the highest performers, low reference inert mass fraction and high ΔV, the percent improvement is higher than when looking at ΔV alone: about 2.2% instead of 1.7%. But low mass efficiency and high ΔV leads to little gain or even loss in some cases.

VI. Non-ideal considerations

This approximately 2% available improvement would be welcome when the technology is ready at scale, but is not mission-making. However, there may be additional improvements available as well:

- *Incorrect/incomplete CEA combustion physics.* If the model does not include certain important species, perhaps not all available heat is released, or components are at a higher molecular weight than actual. In this case, CEA might underpredict. Supposed additional species or reactions are beyond the present scope. Just considering that the lithium is around 4% or less by mass for the highest performing mixtures, it seems like any error here would be unlikely to stronger than **2%**.
- *Combustion-and-expansion efficiency*. One benefit espoused with new propellants such as Li-Al is that the explosive nature of their metal combustion prevents the buildup of large condensed phase particles that cause two-phase flow losses. As mentioned before, the STAR48BV propellant-Isp efficiency is 91.4%. With a 10 cm diameter throat, this is a medium representative of the in-space SRMs class. How much of that shortfall could something like Li-Al be expected to make up? Suppose the following losses are still at play, commensurate with this size of nozzle:
    - Divergence loss (15°) 1.7%
    - Boundary layer loss 1%
    - Kinetics loss 1%
    - Throat erosion loss 1%

    Total loss if no two-phase, 2D losses except divergence = 4.7%
    Efficiency recovery potentially available ≈ **4%**
- *Erosion of nozzle and insulation components*. Due to less slag, lower flame temperature, fuel-rich tendency, or other difference, lithium-aluminum or other novel propellants could possibly be optimized to be significantly less erosive. This could nearly eliminate the throat erosion loss saving another **1%,** and could also improve the inert mass fraction. Mass fraction improvement may be relative to reference f_i, manifesting as a "percent total inert mass saved" in some cases. Another way to mathematically treat it here may be a greater "effective density," as more chamber volume is freed up for propellant.
- *Environmental and economic concerns*. These are beyond the present scope.

For Lithium-Aluminum and other novel propellants, the additional gains due to the various improved efficiencies are estimated at 7% in Isp and ΔV space, and probably exceed 10% in payload at constant ΔV. These would add to the pertinent value from Figure 9 or 10, meaning that potential total improvement may be as high as 12%.

Propellants with encapsulated iron instead of aluminum have also been proposed[vi]. Initial estimates show their ideal *Isp* to be a bit less than aluminized propellant, but the same non-ideal considerations as discussed above could result in favorable performance at some of the mission space.

VII. Conclusions

The ideal rocket algorithm shown allows for more robust propellant performance characterization and optimization than simple Isp, c-star, or density-impulse assessments. Whenever evaluating a new ingredient or propellant family for in-space missions, these calculations can be performed for mass-limited mission types, such as those of interest to NASA for many in-space missions. Similar assessments may be derived for volume-limited spaces. Additional work should be done to further investigate and quantify the non-ideal considerations.

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