

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

PERFORMANCE ENHANCING ADDITIVES FOR HYBRID ROCKETS



Ph.D. THESIS

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Department Aeronautics and Astronautics Engineering

Aeronautics and Astronautics Engineering Programme

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**HİBRİT ROKETLER İÇİN PERFORMANS ARTTIRICI
KATKI MALZEMELERİ**

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FOREWORD

This thesis was written for my Ph.D. degree in Aeronautics and Astronautics Engineering at Istanbul Technical University, Istanbul. The subject of this thesis is related to increasing the performance of hybrid rocket motors by adding energetic materials to the fuel.

After thanking my family for their endless support, I would like to thank a few people here. I am really grateful to my advisor Prof. Dr. Ibrahim ÖZKOL and co-advisor Assoc. Prof. Dr. Arif KARABEYOĞLU for their guidance, reviews and recommendations. These people were always present to help me with my research whenever I needed them. Also, I would like to thank DeltaV Space Technologies and its staff who helped me in the hybrid rocket test operations.

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ABBREVIATIONS

AL	: Aluminium
Mg	: Magnesium
LiAlH₄	: Lithium Aluminium Hydride
NBH₆	: Ammonium Borane
GOX	: Gaseous Oxygen
LOX	: Liquid Oxygen
N₂O	: Nitrous Oxide
Al₂O₃	: Aluminium Oxide
CO	: Carbon Monoxide
CO₂	: Carbon Dioxide
Re	: Reynolds Number
Sci	: Schmidt Number
HTPB	: Hydroxyl-terminated polybutadiene
PMMA	: Poly(methyl methacrylate)
CTE	: Coefficient of thermal expansion



SYMBOLS

I_{sp}	: Specific impulse, s
c^*	: characteristic velocity, m/s
O/F	: Oxidizer to fuel mass ratio
A	: Area, m^2
AR	: Nozzle area ratio, A_e/A_{throat}
t	: Time, s
t_b	: Burn time, s
P	: Pressure, Pa/bar
η	: Efficiency
G	: Mass flux, kg/m^2s
G_{ox}	: Average oxidizer mass flux, kg/m^2s
C_D	: Discharge coefficient
ρ	: Density, kg/m^3
k	: Thermal conductivity, W/m-K
C_p	: Specific heat capacity, J/kg-K
$\dot{\omega}_i$	: Species source term in control surface, kg/m^2s
μ	: Viscosity, kg/m-s
D_{im}	: Effective diffusion coefficient, m^2/s
M_w	: Molecular weight
C_p	: Specific heat capacity, J/kg-K
$\dot{r}$	: Regression rate, mm/s
$\dot{r}_n$	: Nozzle erosion rate, mm/s
ϕ	: c^* equilavence ratio
$\dot{m}$	: Mass flow rate, kg/s
Hz	: Hertz, cycle per second
D_{ti}, D_{tf}	: Initial and final nozzle throat diameter
D_i, D_f	: Initial and final fuel diameter



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PERFORMANCE ENHANCING ADDITIVES FOR HYBRID ROCKETS

SUMMARY

A comprehensive assessment of fuel additives for a paraffin-based hybrid rocket fuel and hybrid rocket test firings are presented in this thesis. The reason for the selection of paraffin wax fuel binder is discussed as well as the expected performance gain by the addition of energetic materials to the fuel. Al, Mg, LiAlH_4 and NBH_6 are selected by assessing the thermochemical calculation results and material availability. An experimental study with liquid nitrous oxide oxidizer is concluded which showed Al and LiAlH_4 are promising materials for future studies. They increase the c^* which in turn increase delivered I_{sp} and decrease the nozzle erosion rate. Also, ammonium borane, which is a promising material because of the rich hydrogen content, is studied, but because of the problems in its procurement detailed tests are postponed in a future study. If the availability and cost problems are solved, ammonium borane is the best choice for theoretical I_{sp} performance. However, it needs to be tested in real operating conditions to better understand its characteristics.

First chapter of the thesis shows that there are improvements of the hybrid rocket regression rate, I_{sp} and combustion efficiency with the energetic material addition. However, the most noteworthy improvement is the nozzle erosion rate reduction. Therefore, it is decided to study this characteristic in more detail.

Due to its relatively low cost and wide availability, carbon graphite is one of the most widely used ablative nozzle material in hybrid rocket propulsion. The erosion characteristics of this material has paramount importance, since it directly influences the I_{sp} performance. This is especially the case for upper stage or in-space rocket motors operating with very long burn times. In this study the effect of aluminum added fuel on the graphite nozzle erosion is studied. In the experimental studies, a high regression rate paraffin-based fuel is loaded with micron size aluminum powder for nozzle erosion reduction. In our approach, aluminum is added at high concentrations as a fuel ring in front of the main paraffin-based fuel which contains no aluminum. Based on the motor tests conducted with gaseous oxygen as an oxidizer, it is shown that aluminum addition decreased the nozzle erosion rate up to 45% and increased the nozzle erosion onset time by 1 to 3 seconds. The new method of introducing an energetic powder in a fuel ring positioned at the fore end of the motor offers an easy and scalable way of reducing the nozzle erosion and improving the I_{sp} performance of the rocket motor.

As pointed out using Al as additive for hybrid rocket motors, substantially reduce the nozzle erosion rate which increase the I_{sp} performance. It is widely available, cost effective and easy to use material. The novel addition of the Al material as a high concentrated ring to the hybrid rocket fuel, makes this method highly scalable for larger rocket motors. In future, ammonium borane additive could be studied, but its cost and availability is a problem to be solved.



HİBRİT ROKETLER İÇİN PERFORMANS ARTTICI KATKI MALZEMELERİ

ÖZET

Bu çalışmada kapsayıcı olacak şekilde, parafin-bazlı hibrit rocket yakıtlarına eklenebilecek katkı malzemelerinin incelemesi yapılmış ve elde edilen bu yeni yakıtlar ile hibrit roket motoru ateşleme testleri yapılmıştır.

Hibrit roketlerin, sıvı ve katı yakıtlı roketlere göre hem üstünlükleri hem de zayıflıkları bulunmaktadır. Hibrit roketlerin en önemli özelliklerinden biri karakteristik olarak çok güvenli olmalarıdır. Ayrıca, yüksek enerji seviyesine sahip sıvı oksitleyiciler kullanabildiklerinden dolayı, katı yakıtlı roketlerden yüksek, sıvı yakıtlı roketlere yakın I_{sp} performansına sahiptirler. Hibrit roket yakıtları genellikle katı fazda olduğundan dolayı yakıtın içerisine katkı malzemelerinin eklenmesi mümkün olmaktadır. Bu katkı malzemeleri, katı yakıt hazırlanırken üretim sürecine dahil edilerek kolaylık ile eklenebilmektedir. Bu çalışmada da bu yöntem ile hibrit roketlerin performansının artırılması hedeflenmektedir.

Referans hibrit roket yakıtı olarak parafin-bazlı yakıt kullanılmıştır. Bunun nedeni parafin-bazlı yakıtların, hibrit roket motorlarının yanma hızını, geleneksel polimerik yakıtlara göre 3-5 kat arası arttırmasıdır. Oksitleyici olarak ise gaz/sıvı oksijen ve sıvı azot protoksit kullanılmıştır. Bu iki oksitleyici de çok rahatlıkla temin edilebilen ve testler sırasında kolay kullanılabilen malzemelerdir. Gaz/sıvı oksijen daha yüksek bir enerji seviyesine sahipken, azot protoksit özellikle depolama gerektiren durumlarda kullanılan bir oksitleyicidir.

Hibrit roket yakıt katkısı olarak kullanılabilecek malzemeler çok geniştir. Plastikten tahtaya, metallerden metal hidrürlere ve organik malzemelere kadar geniş bir katkı malzemesi seçeneği bulunmaktadır. Biz çalışmamızda alüminyum, magnezyum, lityum alüminyum hidrür, amonyum boran ve bor malzemelerine odaklandık. Bu malzemelerin hibrit roket motorunda kullanılması ile elde edilecek teorik ve deneysel performansları incelenmiştir.

Teorik hibrit roket motor hesapları NASA'nın geliştirdiği Chemical Equilibrium with Applications (CEA) programı ve kendi geliştirdiğimiz hibrit roket motor performans hesap programı ile yapılmıştır. CEA programı bize roket yakıt ve oksitleyici karışımının c^* ve CF gibi önemli katsayılarını vermektedir. Bu değerler kullanılarak roketin iç basıncı, yanma verimi ve itki değeri hesaplanabilmektedir. Daha önce bahsettiğimiz hibrit roket yakıtı katkı malzemelerinin teorik olarak vereceği performans etkisi, bu programlar ile hesaplanmıştır. Teorik hesaplar göstermiştir ki, gaz/sıvı oksijen kullanan bir roket motorunun I_{sp} performansı lityum alüminyum hidrür ve amonyum boran kullanıldığında artmaktadır. Azot protoksit kullanan hibrit roket motorunun I_{sp} performansı ise MgB_2 ve AlB_{12} katkılarının dışında diğer katkı malzemeleri ile artmaktadır.

Teorik hesaplamalardan elde edilen ön bilgilerden sonra deneysel çalışmaya geçilmiştir. Öncelikle azot protoksit oksitleyici kullanan 3.1 cm dış çapında yakıtı olan

bir hibrit roket motoru ile testler yapılmıştır. Bu testler ile yakıt yanma hızı, I_{sp} değeri, motor iç basıncı ve nozül erozyon hızı elde edilmiştir. Testler sırasında referans parafin-bazlı yakıtlar “spin-cast” dediğimiz, parafin sıvı haldeyken döndürme yöntemi ile hazırlanmıştır. Katkı malzemeleri ise parafin sıvı halde iken eklenmiş ve kat kat olacak şekilde silindirik bir kaba dökülerek hazırlanmıştır. Motor montajı yapılmadan önce bu yakıtlar istenilen ölçülere göre tornada işletilmiştir.

Azot protoksit testlerinde görülmüştür ki katkı malzemeleri ile elde edilen en önemli performans artışı nozül erozyon hızının kayda değer miktarda azalmasıdır. Yakıt yanma hızında kayda değer bir artış gözlenmemiştir. I_{sp} performansı alüminyum ve lityum alüminyum hidrür ile artmaktadır, fakat bu artışı daha iyi anlamak için test sayısının artırılması gerekmektedir. Sonuç olarak azot protoksit testlerinde görülmüştür ki en önemli etki nozül erozyon hızında olmuştur. Bu karakteristiğin daha iyi anlaşılması için de daha büyük çapta, daha uzun süre yanma sürelerine sahip bir hibrit roket test sistemi hazırlanmıştır. Bu test sistemi oksitleyici olarak gaz oksijen kullanmakta ve 6.5 cm dış çapında yakıtı olan bir roket motoru bulundurmaktadır. Yanma süresinin artırılması ve oksitleyici olarak gaz oksijen kullanılmasından dolayı nozül erozyonu artmış ve farklı yakıtların etkileri daha doğru bir şekilde ölçülmüştür.

Bu testler için hazırlanan test sistemi DeltaV Uzay Teknolojileri A.Ş.’nin yardımı ile kurulmuştur. Oksitleyici olarak kullanılan gaz oksijen bir basınçlı tanktan motorun içerisine akmaktadır. Bu basınçlı tank içerisinde 200 bar civarında olan gaz oksijen, bir basınç regülatörü ile 50 – 60 bar basıncında motora gönderilmektedir. Basınç regülatörü ile motor arasında bir adet ana akış vanası, 2 adet basınç sensörü, 1 adet sıcaklık sensörü, akış kütle debisi ölçümü için orifis ve geri akış önleme vanası bulunmaktadır. Gaz oksijen kütle debisi basınç sensörleri ve orifis yardımı ile, boğulmuş akış (choked flow) hesapları ile bulunmaktadır. Orifiste boğulmuş akış gözlemlendiği ve tanktan gelen basınç sabit bir şekilde verildiğinden, test boyunca oksitleyici kütle debisi sabittir. Test sırasında önemli bir değer olan motor iç basıncı da motorun ön yanma odasına yerleştirilen basınç sensörü ile ölçülmektedir. Motor iç basınç değeri yanma verimi, itki hesabı ve nozül erozyon hesaplarında kullanılan önemli bir değerdir. Tezde de bahsedildiği gibi motor iç basıncı incelenerek nozül erozyonunun nerede başladığı ile ilgili de bilgi edinilebilmektedir. Son olarak ise motor itkisi bir yük hücresi ile ölçülmektedir.

Hibrit roket motoru yakıt katkılarının temini için de bir çalışma yapılmıştır. Bu katkılardan en kolay, ucuz ve hızlıca elde edilebileni alüminyum tozu olmuştur. Yurtiçinde birden çok farklı firma bu tozu temin edebilmekte ve farklı boyut ve şekillerde alüminyum tozu verebilmektedir. Biz bu çalışma için 3 µm boyutunda, küresel şekilde olan alüminyum tozu kullandık. Magnezyum tozunu gerekli evraklar hazırlanarak yurtiçinden alımı sağlanabilmektedir. Magnezyum tozu patlayıcı yapımında da kullanılabildiği için özel izin ile alabilmekteyiz. Lityum alüminyum hidrür yurtdışından, Merck firmasından alınmıştır. Bir önceki diğer iki malzemeye göre fiyatı çok daha yüksektir, gramı 2.5 – 3\$ arasındadır. Bu yüzden ufak miktarlarda alınabilmektedir ve test sayısı düşüktür. Katkı malzemeleri arasında en zor ve pahalı şekilde elde edilebileni amonyum borandır (NBH_6). Bu malzeme öncelikle yurtdışından elde edinilmek istenmiş, fakat fiyat olarak çok yüksek meblağlar istenildiğinden dolayı yurtiçi temin seçenekleri araştırılmıştır. 3 üniversite ve 1 özel sektör olacak şekilde, farklı yerler ile görüşülmüştür. Son olarak “Koç Üniversitesi Bor Tabanlı Malzemeler ve İleri Teknoloji Kimyasallar Uygulama ve Araştırma Merkezi” ile görüşülerek az miktarda amonyum boran temini yapılmıştır. Amonyum

boranın gram maliyeti 5 – 6 \$ arasında olmuştur. Lityum alüminyum hidrürde olduğu gibi maliyet dolayısı ile amonyum boran ile de az miktarda test gerçekleştirilebilmiştir.

Hibrit roket motoru yakıt katkılarının temininden sonra ise bu malzemeleri parafin-bazlı yakıtı eklemek ile de ilgili önemli çalışmalar yapılmıştır. Daha önce belirttiğimiz gibi katkı maddeleri parafin yakıt sıvı halde iken karıştırılarak eklenilmiş ve kat kat olacak şekilde döküm yapılmıştır. Metal tozlu katkı maddeleri, alüminyum gibi, bir sorunla karşılaşmadan rahatlıkla hazırlanmıştır. Metal hidrür katkı maddeleri ise döküm sırasında sıvı yakıtın sıcaklığı nedeni ile hidrojen salınımı yapabilmektedir. Hidrojen salınımını önlemek için metal hidrür katkı maddeleri sıvı yakıt eklenirken, sıcaklık 90 C⁰ altında tutulmuştur. Ayrıca, lityum alüminyum hidrür içeren yakıtlar, ateşleme zamanına kadar kapalı bir kaptaki, nemden uzak olacak şekilde saklanmıştır.

Roket motoru testleri yapılırken toplamda 3 adet basınç, 1 adet sıcaklık ve itki için yük hücresi dataları alınmıştır. Test öncesi ve sonrasında kullanılan yakıtların hem kütleleri hem de iç çap, dış çap ve uzunluk değerleri alınmıştır. Nozül erozyon hızı hesabı için de test öncesi ve sonrasında nozül boğaz çapı ölçülmüştür. Roket motoru testinin ateşleyicisi olarak 4 g civarında bir pirojenik yakıt kullanılmıştır. Öncelikle bu pirojen nikrom tel yardımı ile ateşlenmiş, 3 saniye sonra ise ana oksitleyici vanası açılarak motor ateşlemesi gerçekleştirilmiştir. Test sonrası alınan datalar ile sistem analizi yapılarak yakıt yanma hızı, motor verimi, I_{sp}, itki ve nozül erozyon hızları hesaplanmıştır.

Gaz oksijen test sonuçları incelendiğinde alüminyum katkısı ile nozül erozyon hızının %45 civarında azaldığı ve nozül erozyon başlangıç zamanının da 1 ile 3 saniye arasında ertelendiği görülmüştür. Ayrıca, alüminyum katkısı daha büyük roket yakıtlarında da rahatlıkla kullanılacak şekilde yüksek yoğunluklu bir yüzük şeklinde ana yakıtı eklenmiştir. Bu yeni yakıt katkısı ekleme yöntemi yakıt döküm sürecini hem kolaylaştırmış hem de hızlandırmıştır. Yüzük yakıt şeklinde eklenen bu yüksek yoğunluklu alüminyum yakıtın, ana yakıtı göre bir miktar daha yavaş yandığı görülmüştür. Motor iç basınç grafiklerine bakıldığında, bu yöntemin motor yanma stabilitesine kötü yönde bir etkisinin olmadığı görülmüştür.

Toplayacak olursak, hibrit roket yakıtına eklenen performansı artırıcı katkı maddelerinin en önemli faydası nozül erozyon hızını kayda değer miktarda azaltmasıdır. Özellikle, uzun operasyon süresi olan üst kademe hibrit roket motorları için nozül erozyonunun azaltılması çok önemlidir. Alüminyum tozunun kolay ve ucuz elde edilebilen bir katkı malzeme olmasından dolayı da hibrit roket sistemlerinde bu metodun kullanılmasının çekici olacağını düşünüyoruz. Ayrıca, bu tez çalışması sırasında geliştirilmiş olan yüksek katkı malzemesi yoğunluklu yüzük yakıt metodu da büyük hibrit roket sistemleri için süreci çok kolay hale getirmektedir. Bu çalışmada ortaya çıkartılan teknolojinin hibrit roket sistemleri için çok önemli bir değer olduğunu görmekte ve ileride daha büyük roket motorlarında kullanılacağını düşünmekteyiz.



1. INTRODUCTION

Hybrid-propellant rockets generate thrust by chemically combusting propellants which are in different phases, (i.e. liquid oxidizer and a solid fuel). Conventional hybrid rocket motors use a liquid or gaseous oxidizer and a solid fuel grain such as liquid oxygen and HTPB (Hydroxyl-terminated polybutadiene). The heat transfer from the combustion region to the solid fuel surface vaporizes the fuel while the pressurized oxidizer is injected into the combustion chamber. Liquid nitrous oxide and gaseous oxygen are used as an oxidizer in a simple hybrid rocket configuration, whereas liquid oxygen is used in situations where performance is critical with the cost of handling a cryogenic liquid. HTPB (Hydroxyl-terminated polybutadiene) and paraffin-based fuels are used as solid fuel in most of the applications which are widely available, cost effective and easy to handle. The combination of these propellants gives hybrid rocket motors a specific impulse (I_{sp}) value between liquid bi-propellant chemical rocket systems and solid rocket systems. Also, hybrid propulsion systems present attractive characteristics compared to solid and liquid rocket motors by offering design simplicity, full thrust control capability, safe operation and reduced development costs.

Table 1.1 : Comparisons of different type of rocket systems.

	Liquid Rockets	Solid Rockets	Hybrid Rockets
Performance	Very high performance can be achieved with LOX and H_2	Performance is reduced due to only solid oxidizers	A similar performance as hydrocarbon fueled liquid rockets
Safety	Special care is required to keep the two liquids separate	High explosion possibility if not handled correctly	Nearly zero explosion possibility
Development	Complex system requires long and costly development process	Because of the safety concerns, development is costly	Low development cost and time because of the system simplicity and safety
Operation	Throttleable and start-stop capable. Complex operation.	Not throttleable. Simple operation.	Throttleable and start-stop capable. Simple operation.

The main characteristic differences of the liquid, solid and hybrid rocket systems can be seen in Table 1.1. Also, the rocket configurations with the important system placements can be seen in Figure 1.1, Figure 1.2 and Figure 1.3.

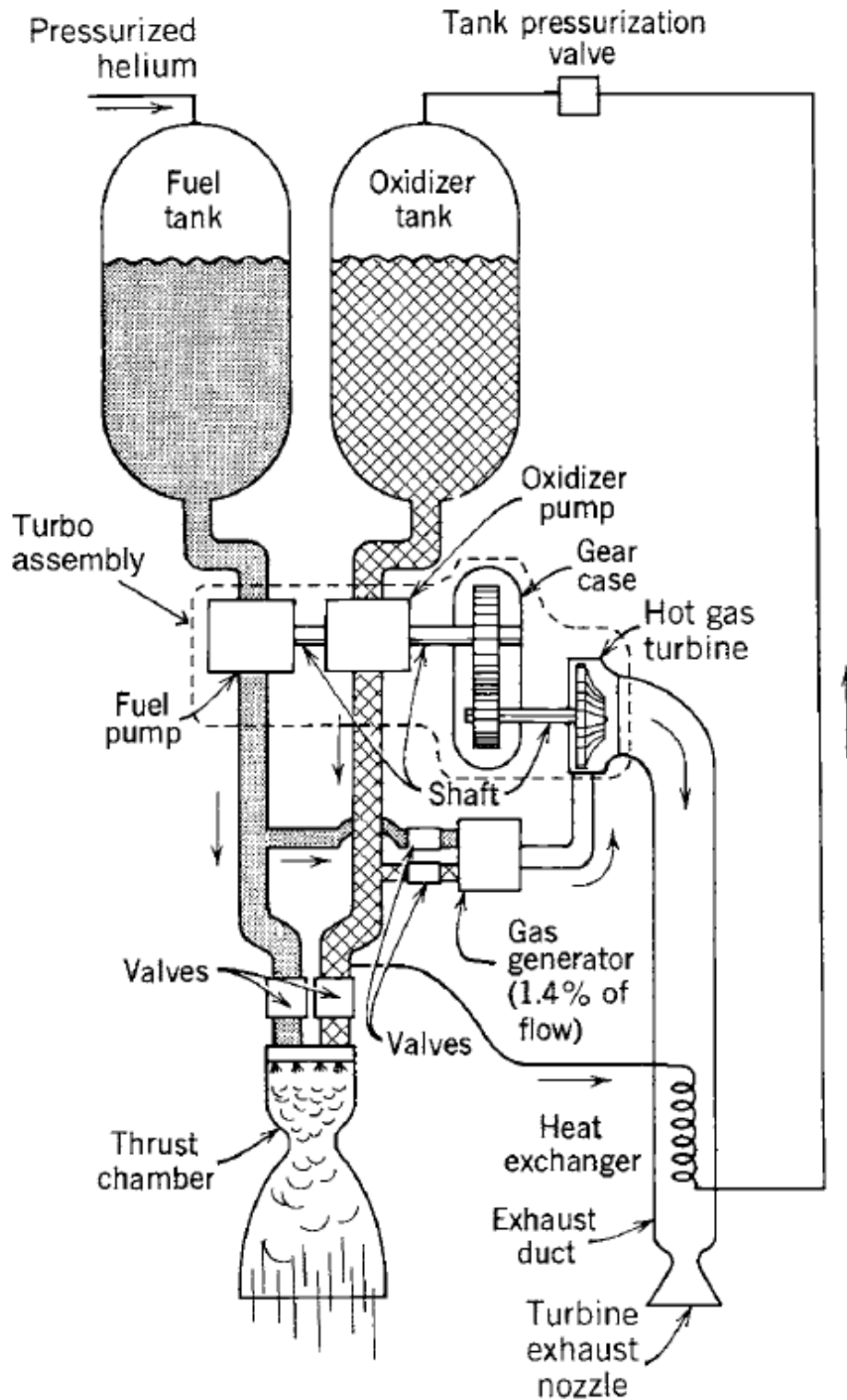


Figure 1.1 : A liquid rocket motor schematic diagram with turbopump feed system and a gas generator [1].

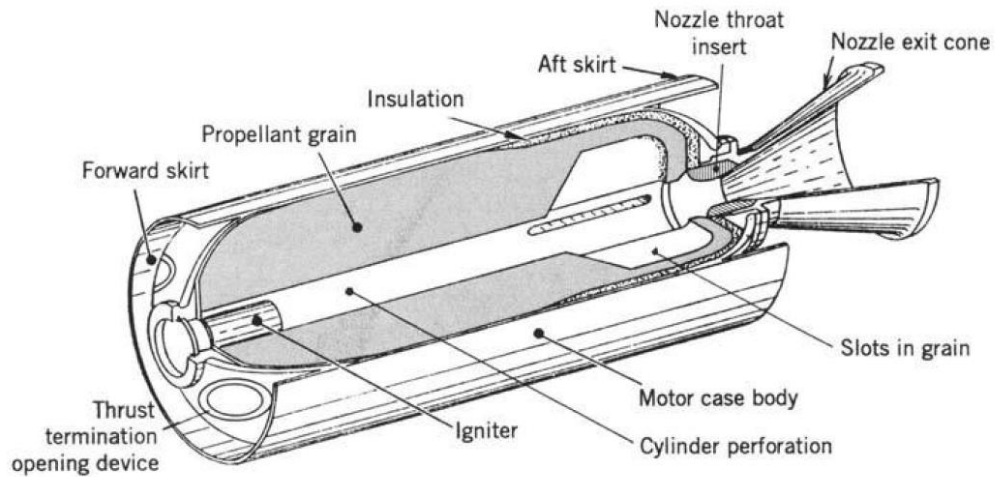


Figure 1.2 : Simplified schematic of a solid rocket motor with a cylindrical propellant grain [1].

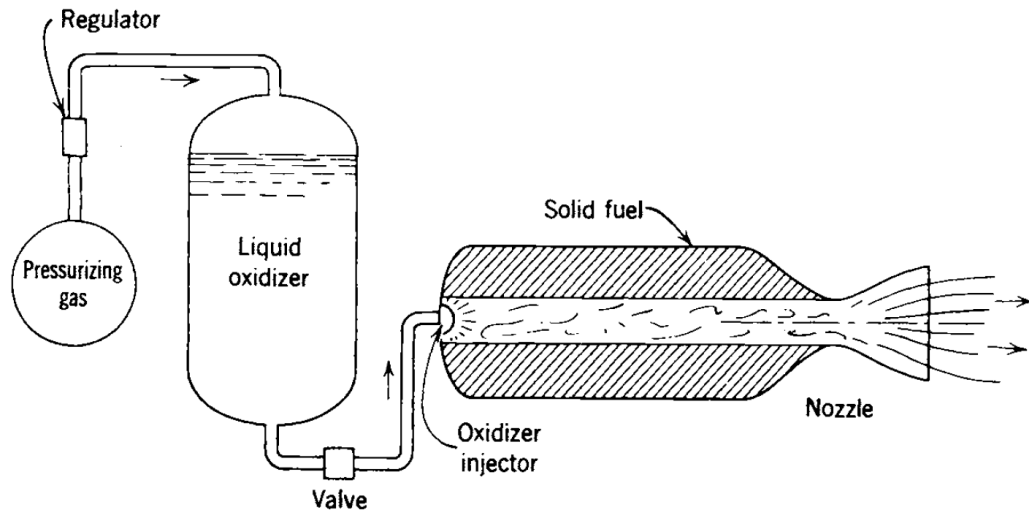


Figure 1.3 : Simplified schematic of a hybrid rocket motor with liquid oxidizer and solid fuel [1].

One very significant disadvantage of conventional hybrid rockets is very low fuel regression rates. This characteristic leads to low thrust densities, complex fuel grain designs and poor fuel loading. Paraffin-based fuels show three to five times higher regression rate at similar mass fluxes compared to polymers such as HTPB due to liquefying characteristics of paraffin-based fuels [2]. When the paraffin-based fuel burns, it produces a liquid layer on the fuel surface which has low viscosity and low surface tension. This liquid layer becomes unstable by the oxidizer gas flow in the port and this instability leads to the lift-off of fuel droplets from the surface increasing the overall mass transfer rate. The combustion mechanism for the liquefying fuel can be

seen in Figure 1.4. In a conventional non-liquefying fuel combustion, there is no liquid droplet entrainment to the combustion chamber and because of that the classical diffusion-limited regression of the fuel is dominant.

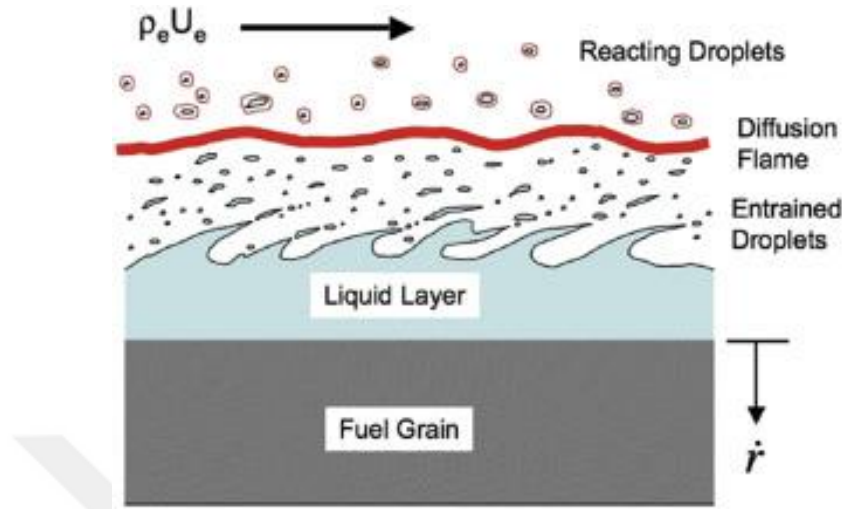


Figure 1.4 : Liquefying hybrid rocket fuel entrainment mechanism [3].

The different fuel and oxidizer combinations for a hybrid rocket is given in Table 1.2. As can be seen, most of the oxidizers and all of the fuels given in Table 1.2 is non-toxic, widely available and easy to handle. The opportunity to use liquid oxygen (LOX) which is a very high-performance oxidizer is an important characteristic.

Table 1.2 : Conventional fuels and oxidizers for hybrid rocket motors.

Fuels	Oxidizers
Polymers (Polyethylene, Plexiglass, Nylon, Rubbers)	Liquid and Gaseous Oxygen
Wood	H ₂ O ₂
Thrash	N ₂ O
Wax	N ₂ O ₄

Even though the liquefying solid fuels substantially increase the regression rate for the hybrid rocket motors, there is still room for improvement by adding energetic materials to the solid fuel grain. There is considerable amount of study in this area and some of them can be seen in Ref. 4 to 10 [4-10]. Also, energetic material addition to the hybrid rocket motor solid fuel such as aluminum (AL), ammonium borane (BH₃NH₃) or lithium aluminum hydride (LiALH₄) can alter the Isp performance as well as the nozzle erosion rate and combustion efficiency.

1.1 Purpose of Thesis

The objective and scope of this study is to increase the performance characteristics of the hybrid rocket motors by using various energetic material additives such as BH_3NH_3 , LiAlH_4 , Al , boron (B), Mg and AlB_{12} . The key performance indicators are the specific impulse, regression rate, nozzle erosion rate and combustion efficiency. Theoretical internal ballistic calculations and experimental hybrid rocket combustion tests are carried out to determine the effectiveness of using performance enhancing additives. Thermochemical ballistic calculations are compared to experimental results to evaluate the effect of these additives to the combustion efficiency.

The unique aspect of this research is to obtain a comprehensive knowledge of the effects of performance enhancing additives to the hybrid rocket characteristics. This research will generate comprehensive comparison of using various kind of materials as additives for hybrid rocket fuel, which would in future can be used to increase rocket performance. Currently there are considerable amount of work to evaluate these additives performances as hybrid rocket fuel ingredients but there is no coherent and comprehensive published work. The research aims to generate a result that clearly shows the advantages and disadvantages of using additives by using theoretical and experimental studies.

This research would greatly contribute to the development of the national space program by increasing and improving the space and launch vehicles' propulsion systems. Identifying and characterizing the possible performance gain related to the performance enhancing additives for hybrid rocket engines will help the future propulsion engineers to design better rocket motors.

1.2 Literature Review

Hybrid rocket motors are an attractive subject for researchers. This is because of the safety and low-cost characteristics of the hybrid rockets which makes developing these systems relatively easily. However, these studies differ in many aspects such as the selection of binders, oxidizers, additive material types and also test setup capabilities. Therefore, we aimed to generate a comprehensive study by using the same set of tools and setups to conveniently compare the different energetic materials' effects to the hybrid rocket motors performance.

Hybrids have been the best type of rocket to benefit a potential performance increase by addition of energetic materials to the solid fuel because most energetic fuel additives are in solid phase under ambient conditions and all high energy oxidizers are naturally in liquid phase [2]. One of the early published works which studies solid fuel additives to the hybrid rocket motor is presented by AMROC personnel in early 1990's³. Two of the fuels had performance additives in them (HTPB/%20 Al and HTPB/40%Li/15%LiH). The other two were pure polymers (HTPB and PMMA). The oxidizers for these studies were LF2 and FLOX. These kinds of oxidizers will not be used in our study because of their high toxicity. Some of the results of this study can be seen in Figure 1.5 and Figure 1.6.

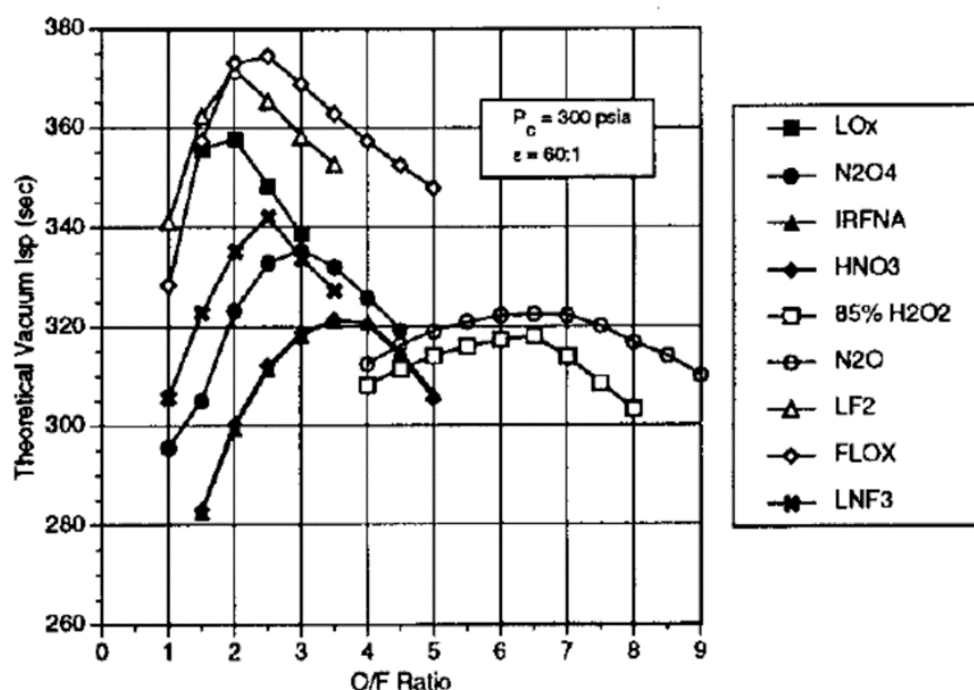


Figure 1.5 : Isp performance of various oxidizers. Fuel is %20 aluminized HTPB [5].

Fuel	Oxidizer	Δ Payload Mass (%)	Average Isp (sec)	Propellant Mass (lb)	Stage Mass Fraction	Stage Volume (ft ³)
HTPB	LO ₂	+11.8	332	104,700	0.864	4,017
HTPB/20%Al	N ₂ O ₄	0	311	105,500	0.871	3,528
HTPB/20% Al	WFNA	-11.5	295	105,800	0.873	3,406
HTPB/20% Al	85% H ₂ O ₂	-14.2	292	105,800	0.873	3,339
HTPB/40%Li/15% LiH	FLOX	+22.9	346	104,600	0.863	4,302

Figure 1.6 : Hybrid upper stage performance for various propellants [5].

A review of metals and other performance additives for hybrid rocket fuels is given by Karabeyoglu. The available energy per unit mass of propellant can be seen in Figure 1.7. As can be seen beryllium is a very energetic material but its toxicity limits its usage. Also, boron is an attractive material, but the ignition and combustion efficiency characteristics are important to get the desired performance increase [4]. One of the most researched energetic materials is aluminium as micro and nano sized particles. It has been shown that aluminium can increase the I_{sp} and regression rate performances as will be discussed later.

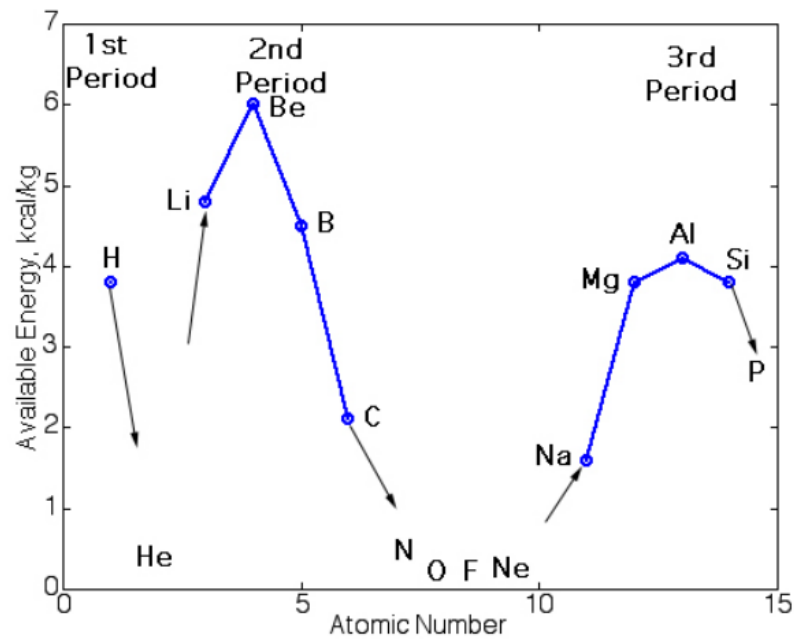


Figure 1.7 : Available energy per unit mass of propellant. Oxidizer is oxygen.

Thermochemical calculations done by Karabeyoglu and Arikan shows detailed performance characteristics of using performance enhancing additives for hybrid rockets in Figure 1.8 and Figure 1.9. It uses paraffin-based fuel and %40 additive concentration for all the cases. The comparison graphs for LOX and N_2O cases can be seen below. It can be seen that ammonia borane (NBH_6) is an attractive additive for hybrid rocket motors with both N_2O and LOX oxidizer. Aluminium has nearly zero effect in LOX cases, but nearly %3 gain in N_2O cases. Lithium aluminium hydride ($LiAlH_4$) presents good performance increase with N_2O oxidizer. Lastly, aluminium hydride seems to be the best additive in terms of I_{sp} and I_v improvement for both cases, but its high cost and low availability presents a drawback for its usage. In our study, we will focus on NBH_6 , $LiAlH_4$, AL and B.

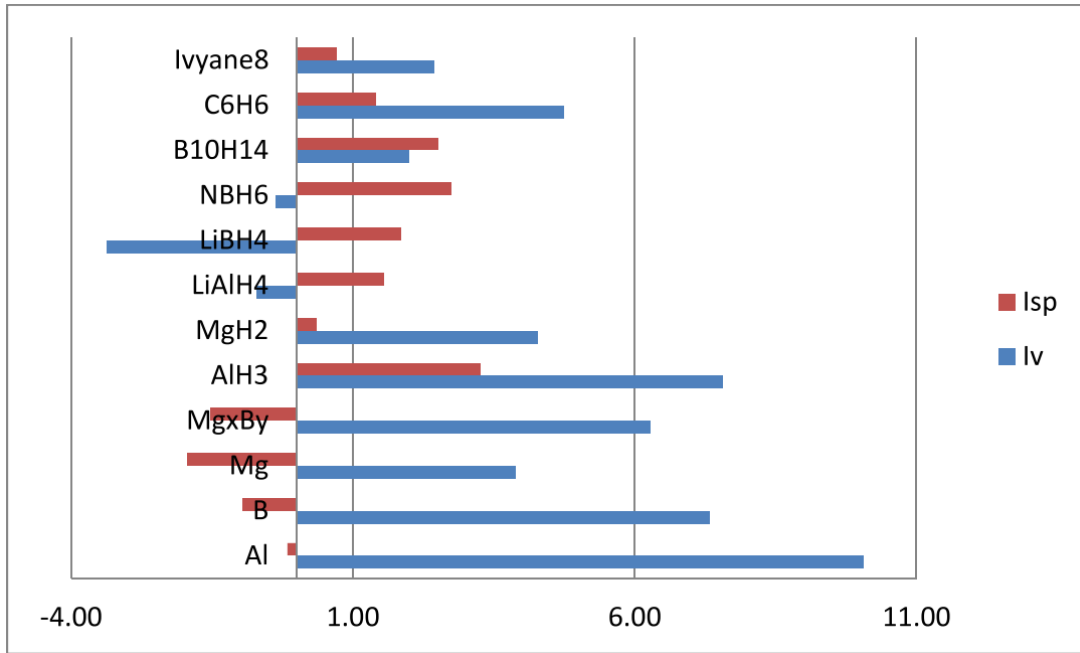


Figure 1.8 : % Isp and Iv improvements for LOX and paraffin-based fuel [4].

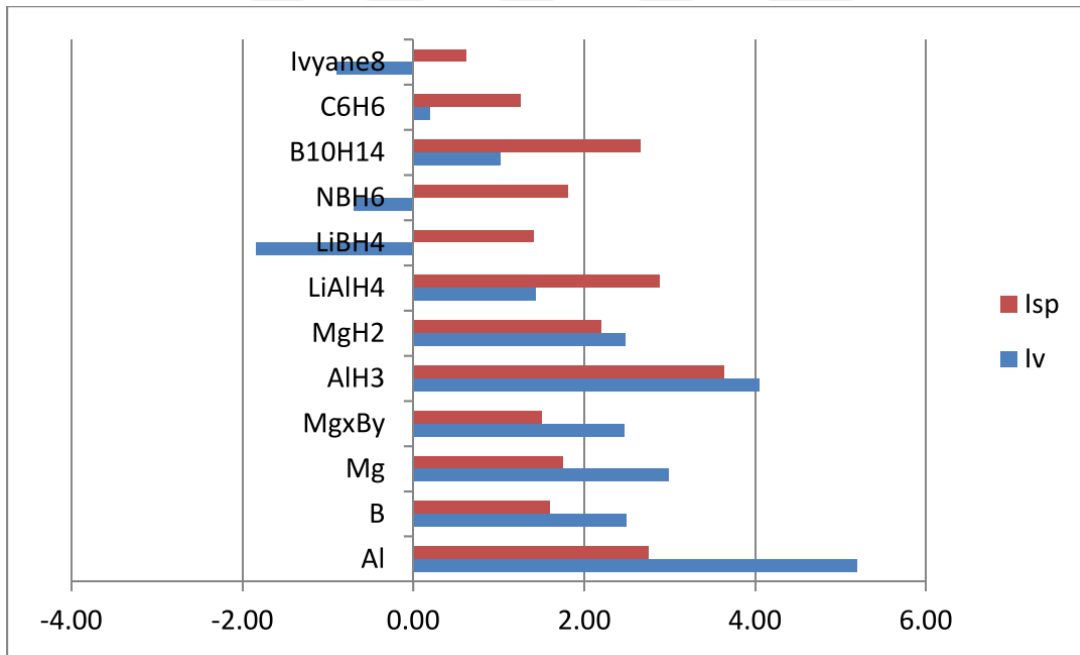


Figure 1.9 : % Isp and Iv improvements for N2O and paraffin-based fuel [4].

As can be seen that experimental studies about the performance enhancing additives for the hybrid rockets are mainly focused on the regression rate characteristics. Some of these works will be discussed in here.

Aluminium-based particle additives are the most researched subject in this area because of the availability, low cost and simple handling of aluminium. George et al

has studied the effect of aluminium addition in the HTPB grains with GOX as oxidizer [6]. Their focus is to increase the regression. Al particle size was 28 microns and additive concentration was approximately 20% by weight. It has been seen that addition of Al particles increased the regression rate of the hybrid rocket motor. However, addition of Al reduced the combustion efficiency from 93% to 89% due to incomplete combustion of the Al particles in the motors with grain lengths ranging from 25 cm to 40 cm.

Kuo, Risha, Evans and Boyer had comprehensive work about addition of aluminium particles to hybrid rockets [7,8,9,10]. In summary they had found that in small scale motors addition of Al particles increased the regression rate for both HTPB and paraffin-based fuel grain configurations. However, large scale experiments did not show any regression rate improvement with Al particle addition.

Akhter and Hassan have tried LiAlH_4 and MgH_2 as additives to 50% HTPB and 50% paraffin wax fuel grain and GOX as the oxidizer [11]. Their work involved characterizing the fuel grains by DSC (Differential Scanning Calorimetry), viscometer and performing the static firing tests. It has been shown that addition of LiAlH_4 and MgH_2 had approximately same regression rate improvement for their case.

The possibility of using ammonia borane (NBH_6) as a fuel additive for hybrid rockets has been considered by Weismiller et al [12]. Paraffin-based fuel grain and GOX oxidizer are used in their study. The addition of ammonia borane in the 10% level improved the regression rate, but concentrations over 20% by mass have resulted in a reduced improvement or even decrease in regression rate. Their c^* efficiency was claimed to be 100% for all formulations and nozzle efficiency was %60. However, both efficiency values are not realistic to believe, so it is believed that the c^* efficiency estimation or measurement is at fault. Also, the regression rate measurements of their tests can be seen in Figure 1.10. As can be seen, the 10% formulation increased the regression rate of the base fuel. Higher than 10% addition of NBH_6 by mass has decreased the regression rate.

Some other important studies about the energetic additives for hybrid rocket fuels are as follows;

The Sandpiper target drone used a hybrid rocket motor with PMMA as main fuel binder and MON-25 as oxidizer. It was operational in the 1960's. This system was

using 10% by mass Mg powder additive in its fuel. They, also, tested some other additives such as Al, B and Be. Since it was a long burning sustainer motor, the regression rate improvement by energetic additives was not the main reason for using additives. It was for I_{sp} improvement.

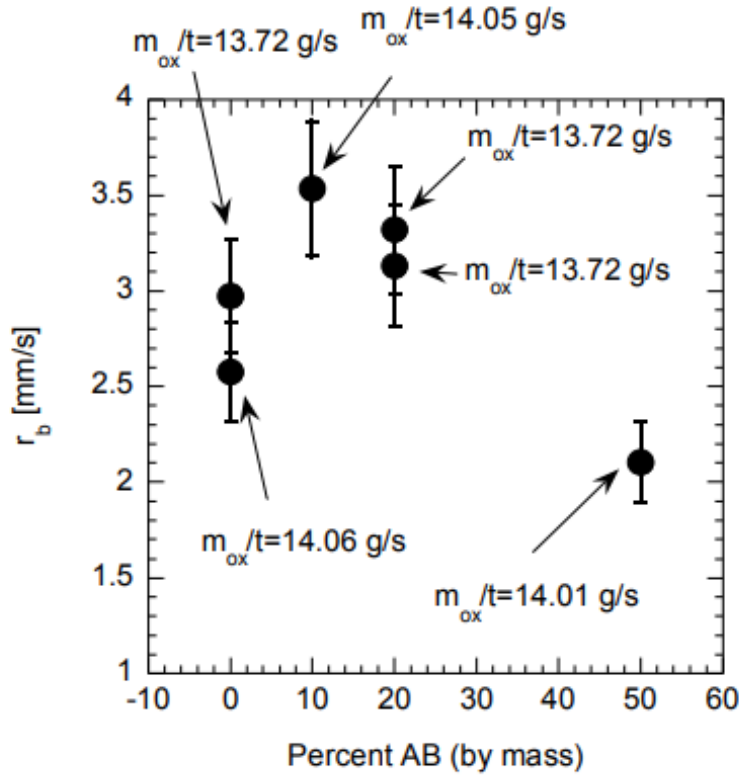


Figure 1.10 : Regression rate vs NBH_6 concentration ratio in fuel [12].

Carmincino et al. [13] have studied MgH_2 and nano-Al additives. They have used HTPB binder in a laboratory scale burner test setup. The nano-Al, they used was an Alex type powder which had an average diameter of 50 nm and it was uncoated. MgH_2 was added %5 by mass and nano-Al was added %15 by mass to the fuel. They have reported that the additives did not increase the regression rate of the HTPB based fuel. They have obtained very high c^* efficiency which is attributed to the slag formation at the nozzle throat. MgH_2 powder tests have shown %5 reduction in c^* efficiency compared to neat HTPB based fuel.

$LiAlH_4$ addition to the paraffin-based hybrid rocket fuel is studied by Larson et al. [14]. They have investigated up to 28% by mass $LiAlH_4$ addition to the fuel in a laboratory scale test system. The oxidizer was gaseous oxygen. They have used a

layered spin casting method for the production of the fuels. These tests had short steady-state durations, which we believe reduced the accuracies of the regression rate measurements. They have found out that the addition of LiAlH_4 did not change the regression rate of the neat paraffin-based fuel.

There was, also, a study about combination of materials used inside the hybrid rocket fuel. One study investigated the performance characteristics of nano sized Al-Cu bimetallic powders inside HTPB binder [15]. In their small tube burner, they have reported that the 15% Al – 85% Cu bimetal addition in HTPB had higher regression rate than ALEX aluminium in HTPB. The addition of material by mass was 10% for both of the cases. However, the resulted I_{sp} performance is lower due to the high molecular weight of Cu. We believe that the the regression rate increase by reducing the I_{sp} performance is not attractive for most cases, so this combination of Al-Cu is not favorable.

As can be seen from the open literature studies that there is no comprehensive research about the performance improvement related to the energetic material addition to the hybrid rocket fuel. Most of the research is revolved around regression rate improvement, but our focus will be more comprehensive.

1.3 Performance Parameters Definition

To better understand the rocket performance characteristics, there are some important parameters to look at and their explanation is given below:

- c^* , (cstar), is the characteristic velocity defined by chamber pressure, throat area and propellant mass flow rate. The reason is so useful is that it can be used to measure the combustion efficiency in terms of relatively easy measured quantities from the test results Equation 1.1. P_c , is chamber pressure, A_t is nozzle throat area and m , is the total mass flow rate.
- I_{sp} , is the specific impulse. It has been defined as the thrust per unit weight flow of propellant. The definition of I_{sp} given in Equation 1.2.
- Regression rate of the fuel is defined in Equation 1.3. D_i , is initial inner fuel diameter and D_f is final fuel diameter and t_b , is the total burn time. It is an important parameter because the thrust is directly related to total propellant mass flow rate given in Equation 1.4.

$$c^* = \frac{P_c A_t}{\dot{m}} \quad (1.1)$$

$$I_{sp} = \frac{T}{\dot{m} g_0} \quad (1.2)$$

$$\bar{r} = \frac{D_i - D_f}{2t_b} \quad (1.3)$$

$$T = \dot{m} c^* C_F \quad (1.4)$$



2. THEORETICAL I_{sp} CALCULATIONS

2.1 Selection of Materials

The selection of the materials is depended upon the characteristics given below:

- Toxic materials are not included in the selection.
- Since there will be an experimental study, availability and cost is an important property.
- No explosion hazard.
- Most promising and practical members of additives are selected from the each of the following groups: metals, metal hydrides and boron compounds.

The selected materials following these characteristics can be seen below. We believe that these materials are, also, the most feasible for operational large scale hybrid rocket motors.

The oxidizers are;

GOX: Gaseous oxygen is a practical and potent oxidizer in a small-scale rocket motor test system. It is widely available, easy to handle and delivers high performance. However, high scale usage of GOX is limited due to very low density. Gaseous oxygen is procured from HABAŞ as single gas cylinder tanks.

$N_2O(L)$: Liquid nitrous oxide is also a practical oxidizer. It has good availability, storability, reasonable cost and most importantly self-pressurization. However, it is a low energy oxidizer because of the nitrogen content and low oxygen mass in the molecule. N_2O_L is, also, procured from HABAŞ as single cylinder tank.

Since the required mass flow rates for the static test firings are between 20 g/s to 100 g/s, the GOX is used directly from the storage tank and N_2O_L is used from a small cylinder tank which is filled up before each test. An example of the storage tanks can be seen below Figure 2.1.

The selected fuel will be discussed, but hybrid rockets have a very wide range of fuel selection. From wood to organic compounds to metals.



Figure 2.1 : Storage tanks for the oxidizers.

The selected fuel is;

Paraffin Waxes: As mentioned before paraffin waxes have the advantage of high regression rate characteristics than polymeric materials. Also, hydrophobic property of paraffin waxes is important for a large number of additives that are sensitive to moisture. In addition, paraffin waxes are low cost, readily available, nontoxic, very long-life time and high performance.

The selected materials for the thermochemical study are: Al, Mg, B, MgB_2 , AlB_{12} , NBH_6 and LiAlH_4 .

2.2 Theoretical Calculations

A theoretical I_{sp} calculation is done with different energetic materials and paraffin-based fuel in this study. In these calculations Chemical Equilibrium Applications (CEA) program from NASA is used for chemical equilibrium calculations. The results can be seen in the table and figures below for gaseous oxygen (GOX) and liquid nitrous oxide (N_2O_L) as oxidizers. Initially, energetic material addition ratio is taken as %40 because higher material addition increases the difficulty of getting a uniform material distribution inside the solid fuel and it increases the cost of the fuel. Especially materials like ammonium borane (NBH_6) and lithium aluminum hydride (LiAlH_4) are expensive because we are buying in smaller quantities. These costs will be reduced if it is supplied in bulk quantities.

As it can be seen in Table 2.1 and Figure 2.2 that the best performing material in terms of I_{sp} is ammonium borane (NBH_6). %40 addition of this material increases the I_{sp} performance of paraffin-based fuel by 2.51% or 5.5 seconds with GOX . This increase

in I_{sp} is worthwhile to investigate and the first experimental tests will be focused on adding NBH_6 to hybrid rocket fuel. Another I_{sp} increase can be seen with $LiALH_4$ addition. Other materials that we studied do not increase the I_{sp} performance of paraffin-based hybrid rocket with GOX as its oxidizer.

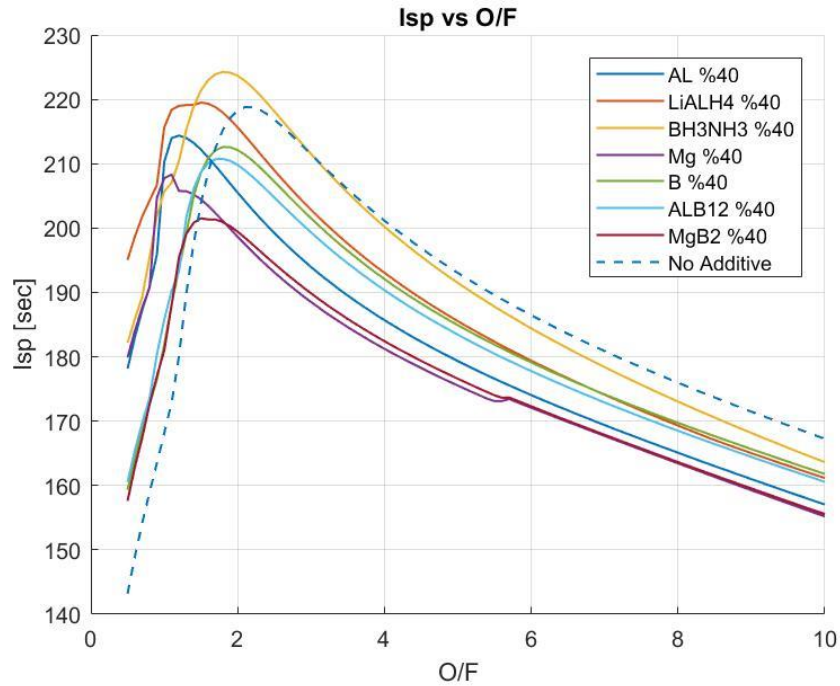


Figure 2.2 : I_{sp} vs O/F results with different energetic material additions to the paraffin-based hybrid rocket solid fuel. Oxidizer is GOX and chamber pressure is 20 bar. Ambient pressure is 1 bar.

Table 2.1 : Theoretical calculation results with GOX.

Performance Value	Reference Fuel	Metals			Metal Hydrides	Boron Compounds		
		AL	Mg	B		BH_3NH_3	ALB_{12}	MgB_2
I_{sp} (second)	218.8	214.4	208.3	212.6	219.5	224.3	210.8	201.5
ΔI_{sp} , seconds	0	-4.4	-10.5	-6.2	0.7	5.5	-8	-17.3
ΔI_{sp} , %	0.00%	-2.01%	-4.80%	-2.83%	0.32%	2.51%	-3.66%	-7.91%
Best O/F ratio	2.15	1.2	1.1	1.8	1.5	1.8	1.8	1.5

The effect of energetic material addition to the hybrid rocket fuels with $N_2O(L)$ as oxidizer can be seen in Table 2.2 and Figure 2.3. Ammonium borane is the best performing one in terms of I_{sp} with $N_2O(L)$. Aluminum is the 2nd best performing one and a very good choice for this case because of lower best O/F ratio and high density of aluminum. Using aluminum as an additive for paraffin-based hybrid rocket fuel with

$\text{N}_2\text{O}(\text{L})$ oxidizer is, also, attractive because aluminum is a low-cost material and highly available. The disadvantages of aluminum addition would be decrease in combustion efficiency and two-phase flow losses in the nozzle.

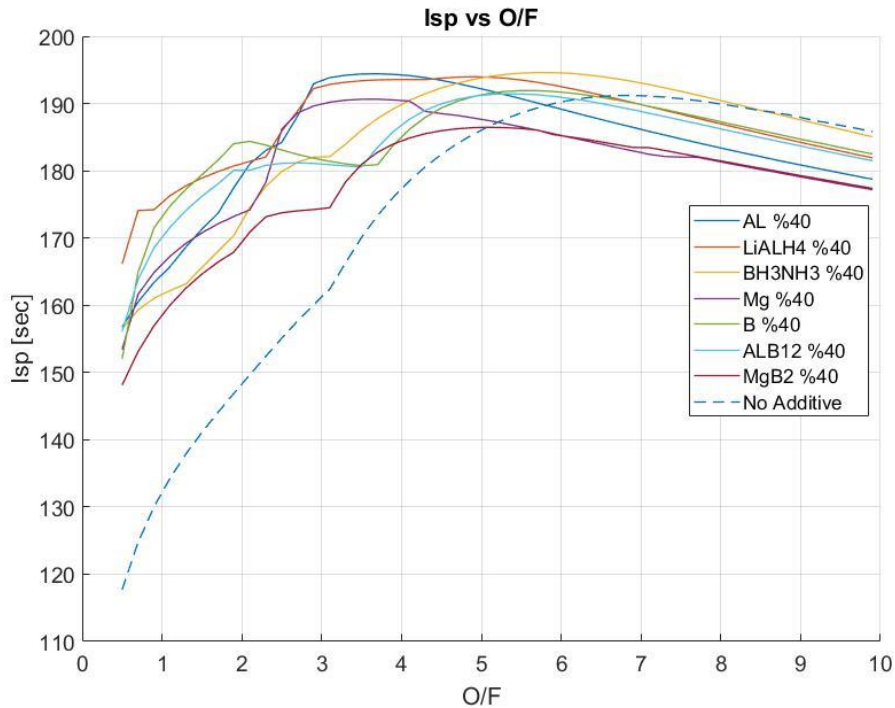


Figure 2.3 : I_{sp} vs O/F results with different energetic material additions to the paraffin-based hybrid rocket solid fuel. Oxidizer is $\text{N}_2\text{O}(\text{L})$ and chamber pressure is 20 bar. Ambient pressure is 1 bar.

Table 2.2 : Theoretical calculation results with $\text{N}_2\text{O}_\text{L}$.

Performance Value	Reference Fuel	Metals			Metal Hydrides	Boron Compounds		
		AL	Mg	B		BH_3NH_3	ALB_{12}	MgB_2
I_{sp} (seconds)	191.2	194.4	190.6	191.9	194	194.6	191.4	186.5
ΔI_{sp} , seconds	0	3.2	-0.6	0.7	2.8	3.4	0.2	-4.7
ΔI_{sp} , %	0.00%	1.67%	-0.3%	0.37%	1.46%	1.78%	0.10%	-2.4%
Best O/F ratio	6.9	3.7	3.7	5.6	4.9	5.8	5.4	5.2

As it is discussed, energetic material addition can increase the I_{sp} performance of the paraffin-based hybrid rocket motors, but just on its own the increase in I_{sp} is not enough to justify the energetic material addition to the hybrid rocket fuel because the relatively low increase in I_{sp} which is nearly %2.5 might not be fully measurable in a real test setup with sensor inaccuracies and combustion efficiency effects. However, there are

other effects of using energetic materials in hybrid rockets to regression rate, nozzle erosion rate and combustion efficiency. In the tests all of these effects are studied.





3. TEST SETUP

3.1 N₂O_L Test Setup with 3.1 cm Fuel Diameter

The hybrid rocket motor test setup has a 3.1 cm outer grain diameter paraffin-based fuel and liquid nitrous oxide (N₂O_L) as oxidizer. The liquid oxidizer is flowing from a small run tank. Since the N₂O_L has a self-pressurizing characteristic, the tests are completed at a specific temperature which is 20 C⁰ and 50 bar. The run tank is filled before each test from the HABAS cylinder storage tank and the mass of the run tank before and after the test is measured. This measurement is used to calculate the average oxidizer mass flow rate. The hybrid rocket motor design and motor test setup for 3.1 cm hybrid rocket motor can be seen in Figure 3.1 and Figure 3.2.

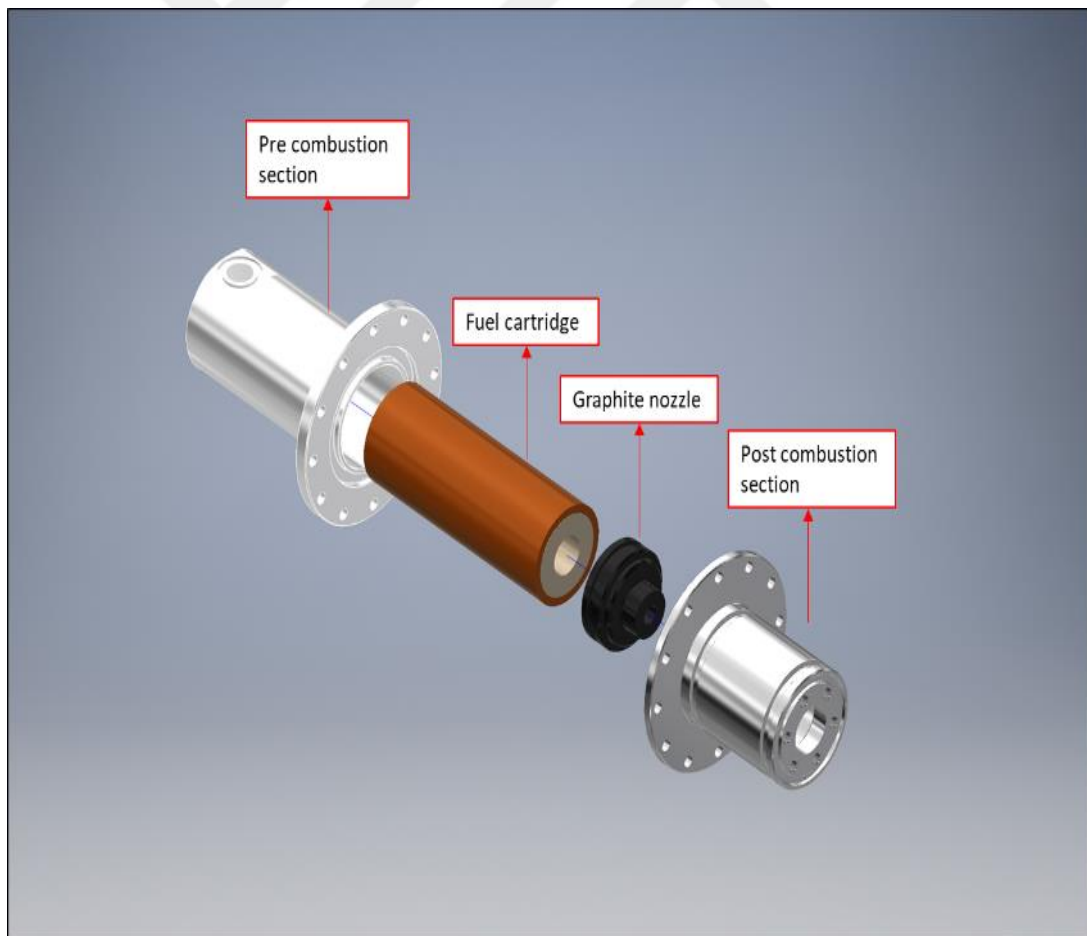


Figure 3.1 : 3.1 cm hybrid rocket motor design. Fuel cartridge and graphite nozzle can be easily changed between tests.

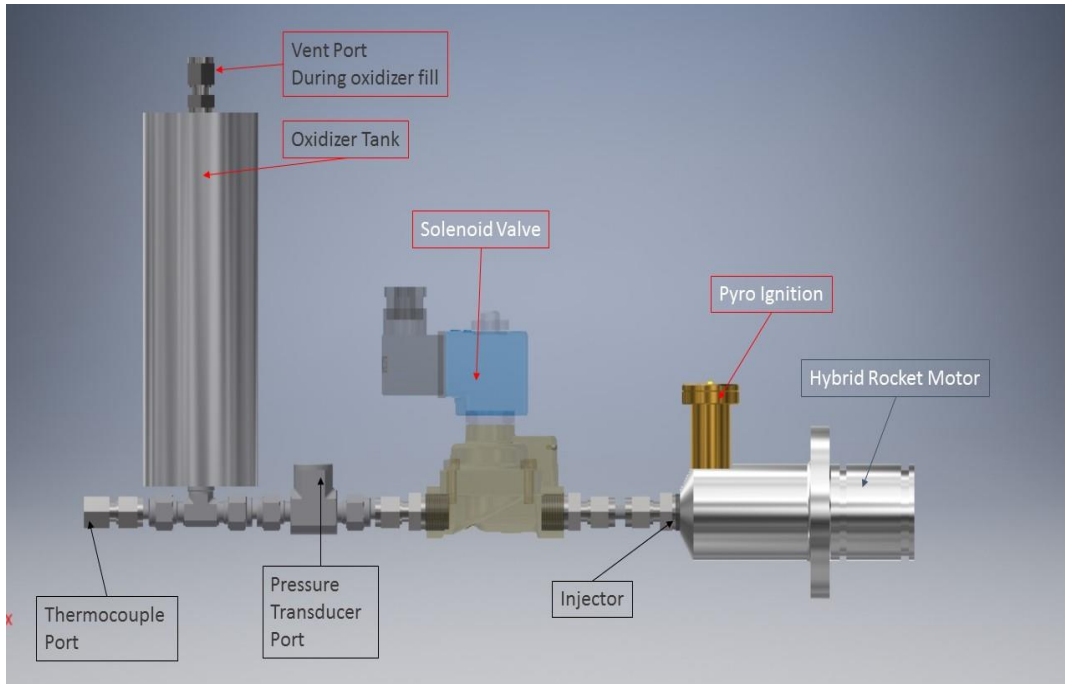


Figure 3.2 : 3.1 cm hybrid rocket motor test setup with liquid N_2O oxidizer. $N_2O(L)$ tank is designed to have 220g to 250g oxidizer depending on the ambient temperature.

The oxidizer mass flow rate calculation for the N_2O_L tests is done by measuring the initial and final tank mass. The combustion chamber pressure is measured by the pressure sensor inside the pre-combustion chamber. Fuel diameter, length and mass is measured before and after the tests to determine the important performance parameters like regression rate. Finally, nozzle throat diameter is measured before and after the tests to determine the nozzle erosion rate. The nozzle was machined from high density graphite with area ratio of 1.0. Since there is no load cell to measure the thrust values obtained from this motor, I_{sp} comparison between different tests will be done by using c^* , combustion efficiency. The c^* value will be obtained by using theoretical calculations and experimental data. An example test firing with N_2O liquid oxidizer can be seen in Figure 3.3.

3.2 Gaseous Oxygen Test Setup with 6.5 cm Fuel Diameter

Our hybrid rocket test facility uses both N_2O_L and gaseous oxygen (GOX) as oxidizer. Gaseous oxygen increases the nozzle erosion rate, so that the nozzle erosion difference between the tests can be seen more clearly. Also, the effect of adding energetic materials to the more energetic oxidizer, GOX, will be studied.

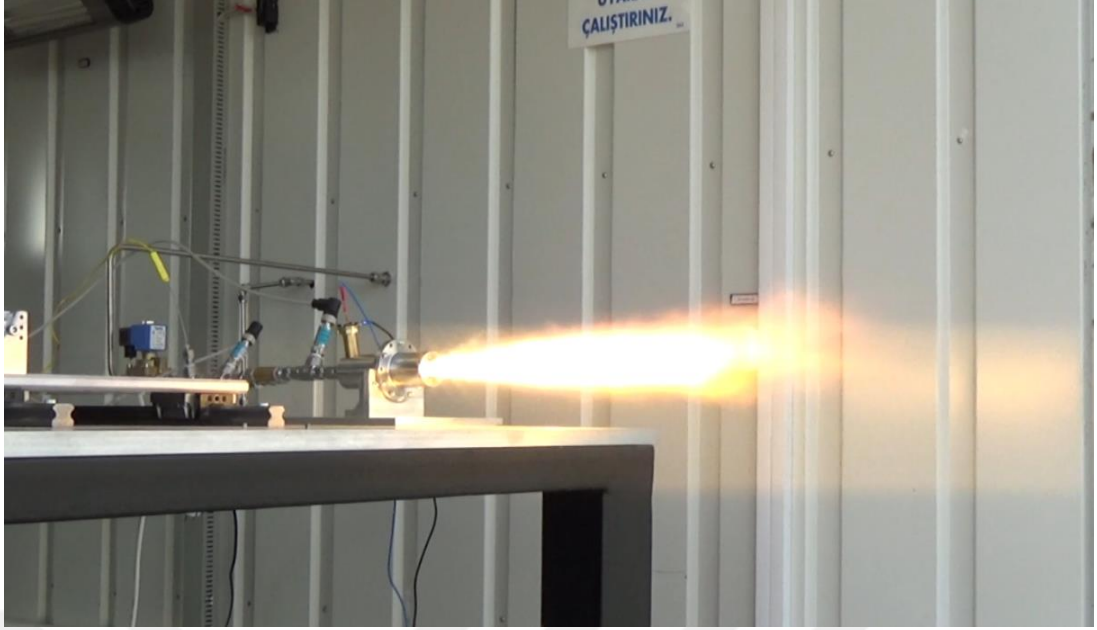


Figure 3.3 : 3.1 cm hybrid rocket motor preliminary test run.

The gaseous oxygen flows from the storage tank directly. The pressure is kept constant by use of a pressure regulator. This regulated pressure determines the oxidizer mass flow rate with a choked orifice. The 6.5 cm hybrid rocket motor design can be seen in Figure 3.4.

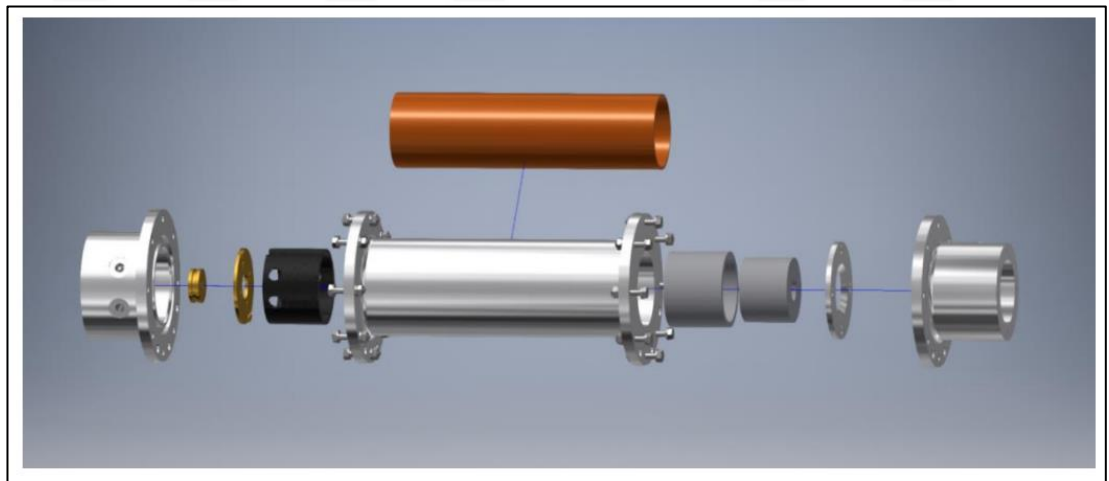


Figure 3.4 : GORTEM 6.5 cm Hybrid Rocket Engine of DeltaV Space Technologies.

The gaseous oxygen-based hybrid rocket test setup can be seen in Figure 3.5. The casing of the hybrid rocket motor, which has an outside diameter of 65 mm, is made out of aluminum and the length of the fuel can be changed by adding different length sections which give us the opportunity to study motors with varying O/F ratio. Ignition is performed by a pyrotechnic igniter, which has approximately 3 grams of solid

propellant and ignition is started by sending a current through a nichrome wire. GOX is taken from a bottle and injected into the motor chamber through a 9.5 mm pipe opening without an injector. Oxidizer mass flow rate is calculated from the pressure and temperature readings taken upstream of a choked orifice. Carbon-graphite nozzle is used with 7 to 10 mm throat diameters to achieve different chamber pressure levels.

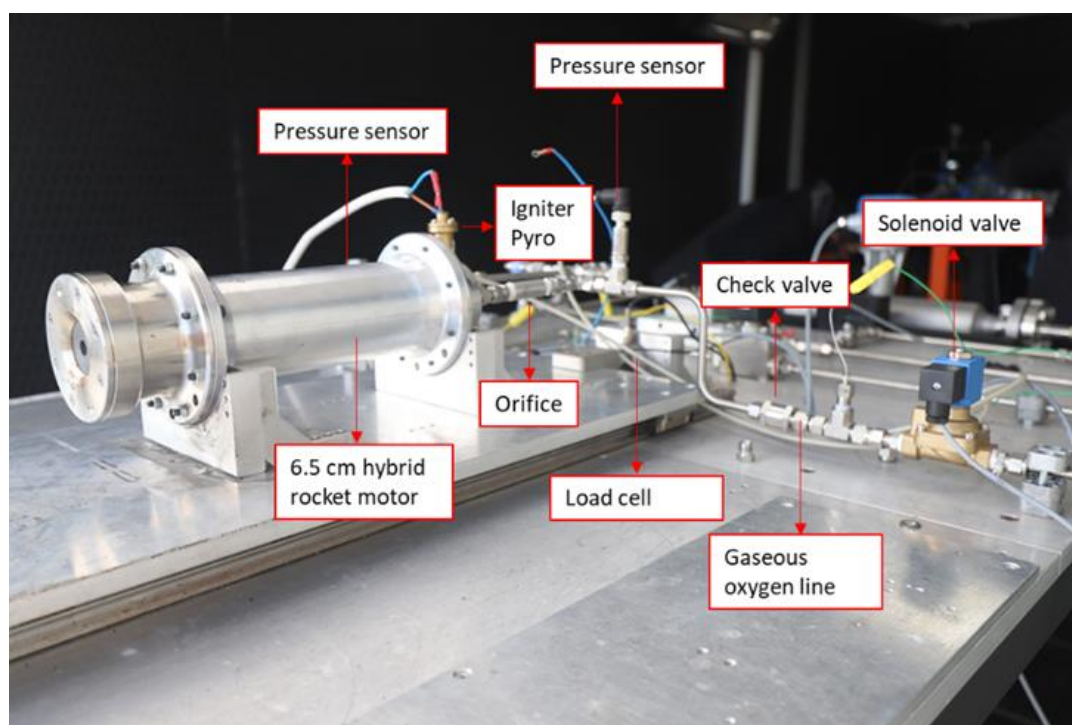


Figure 3.5 : Hybrid rocket motor test setup with GOX as oxidizer. Paraffin-based fuel is used and its outer diameter is 6.5 cm which gives us between 12 to 20 seconds of burn time.

Tank pressure, temperature, line, manifold, and chamber pressures were recorded by using a National Instruments Data Acquisition System (DAQ) and Lab View signal express software. The DAQ sampling rate during the tests is 5120 Hz. A K-type thermocouple is used to measure the temperatures. Pressure transducer has measuring efficiency $\pm 0.5\%$ of the full measurement scale of 70 bars with repeatability that is better than $\pm 0.05\%$. A detailed relative error analysis is given in Appendix A.

3.3 Fuel Preparation

The first step to our hybrid rocket fuel preparation is to melt the pure paraffin slab at appropriate temperature and add the polymeric additives for structural integrity. Without the polymeric additives, the pure paraffin is prone to cracking and structural

degradation during the motor operation. The used paraffin slab can be seen in Figure 3.6. It is in white color before the melting and it becomes transparent when in liquid form. To reduce the radiative heating of the whole fuel during the motor operation, black paraffin dye is added to liquid paraffin.

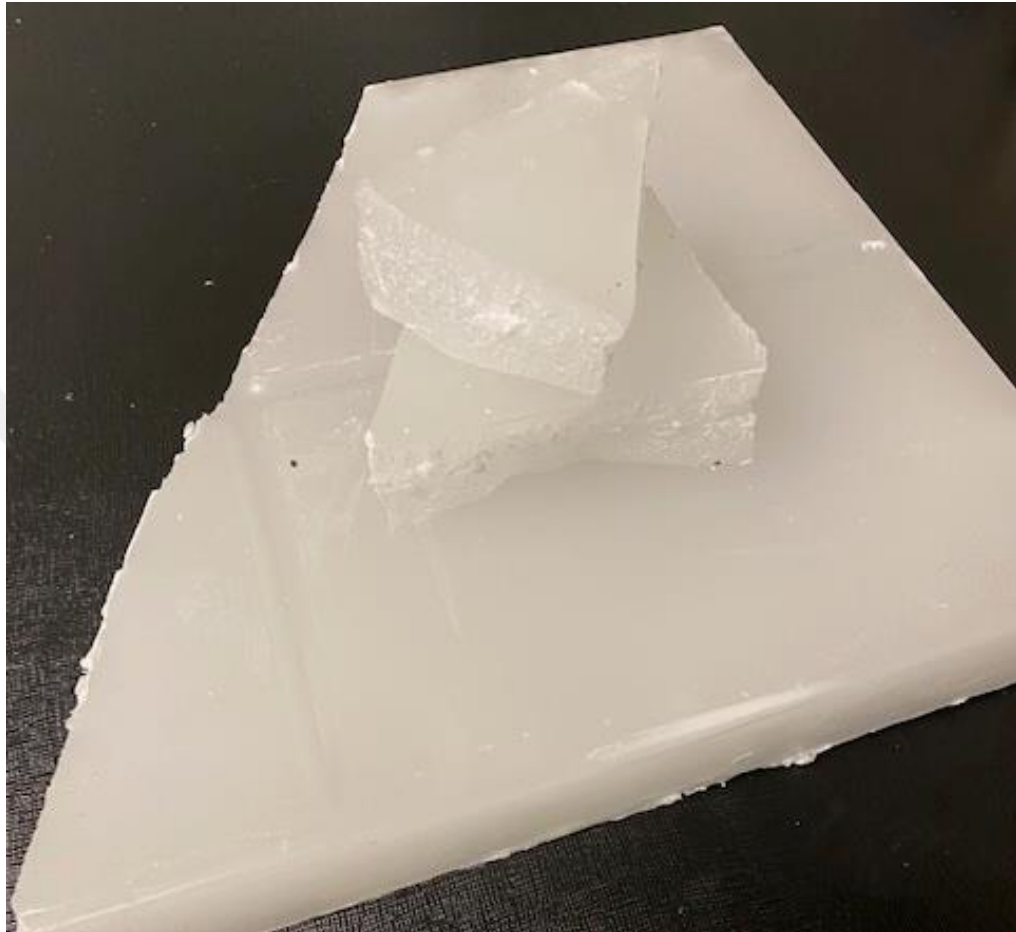


Figure 3.6 : Pure paraffin fuel slab.

The final state of the liquid paraffin-based fuel can be seen in Figure 3.7.

After this step, the liquid fuel is poured into the phenolic fuel case. The poured fuel mass is measured to achieve the desired fuel inner diameter. The phenolic case is held by two end caps and placed it into the spin casting machine. This machine spins the liquid fuel at desired speed. This speed is adjusted to get a structurally safe fuel cartridge without any cracking. The spin casting machine can be seen in Figure 3.8. The resulting fuel shape is a hollow cylinder with desired inner and outer diameter. The inner diameter, outer diameter, length and mass of this fuel is measured, before it is glued to the phenolic casing in order to use these values for performance calculations. The final paraffin-based fuel can be seen in Figure 3.9.



Figure 3.7 : Liquid form of the paraffin-based fuel.



Figure 3.8 : Spin casting machine and phenolic fuel case.



Figure 3.9 : Paraffin-based fuel and phenolic casing.

The hybrid rocket fuel additives that used in our experimental study is Al, Mg, LiAlH_4 and NBH_6 . When preparing a fuel with these additives, we need another method than spin-casting method because these materials are in powder form. The powders are concentrated on the outer diameter of the fuel, when spin casting the fuel. Therefore, the energetic material added fuel is casted layer by layer. This way the fuel composition is uniform along the radial direction, but there might be small non-uniformities along the axial direction, which we can tolerate. The acquired fuel additives and their specifications are given in Table 3.1. The prices are given for the bulk quantities, only the ammonium borane price is given for small quantities because there is no availability for large quantities for now. Also, the pictures of the fuel additives can be seen in Figure 3.10 to Figure 3.12.

Table 3.1 : Fuel additives' specifications.

Fuel Additive Name	Powder size, μm	Supplier	Price, \$/kg
Aluminium	<3	Nanokar Nanotechnology	15
Magnesium	<63	Magnezyum ve Metal Tozlari Ticaret A.Ş.	5
LiAlH_4	-	Merck	250
NBH_6	-	Koç Üniversitesi KABAM	5000

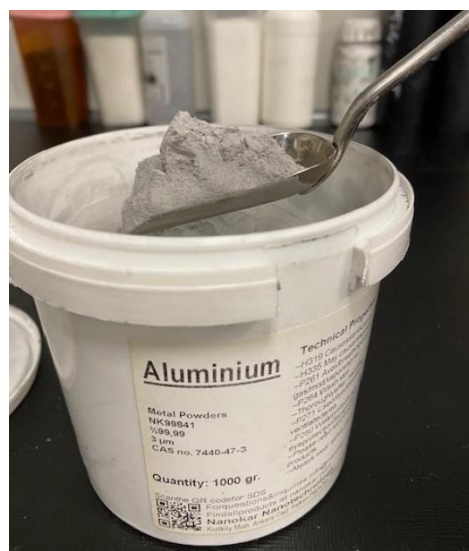


Figure 3.10 : Aluminum powder.

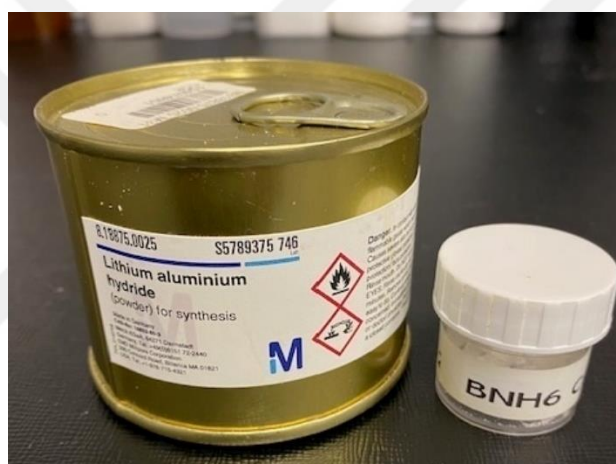


Figure 3.11 : LiAlH_4 and NBH_6 .

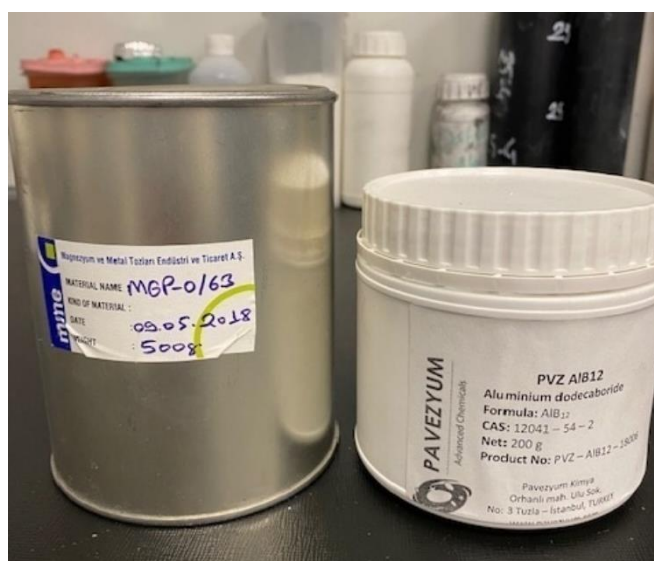


Figure 3.12 : Magnesium powder and AlB_{12} .

4. LIQUID NITROUS OXIDE MOTOR TESTS and RESULTS

An example batch of static motor tests' can be seen in Figure 4.1.

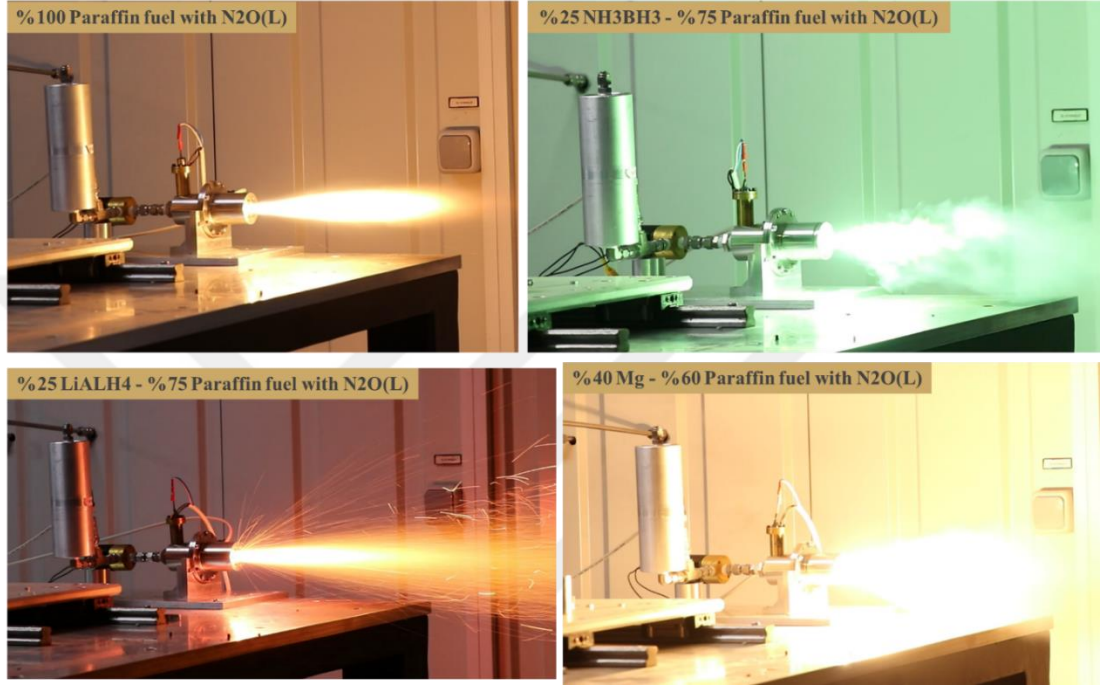


Figure 4.1 : 3.1 cm hybrid rocket static firing test photos with different additives.

The results of a typical pressure trace and important performance parameters for 3.1 cm hybrid rocket test is given in Figure 4.2 and Table 4.1. The average linear regression rate, $\bar{r}$, and average oxidizer mass flux, $\bar{G}_o$, were measured using Equation 4.1 and Equation 4.2. The arithmetic average of the initial, D_i , and final port diameters, D_f , is used in the average oxidizer mass flux calculation which is shown to have lowest rank of error [16]. $\dot{m}_o$, is the average oxidizer mass flow rate.

$$\bar{r} = \frac{D_i - D_f}{2t_b} \quad (4.1)$$

$$\bar{G}_o = \frac{16\dot{m}_o}{\pi(D_i + D_f)^2} \quad (4.2)$$

The characteristic velocity (c^*) or combustion efficiency η_{c^*} is an important test result. Its calculation is done using Equation 4.3. The theoretical c^* value comes from the NASA CEA code [17]. In this equation P_c is the average chamber pressure, A_t is the throat area, C_D is the nozzle discharge coefficient, $\dot{m}_{ox}$ and $\dot{m}_{fuel}$ are average oxidizer and fuel mass flow rate.

$$\overline{\eta_{c^*}} = \frac{P_c A_t C_D}{(\dot{m}_{ox} + \dot{m}_{fuel}) c_{theoretical}^*} \quad (4.3)$$

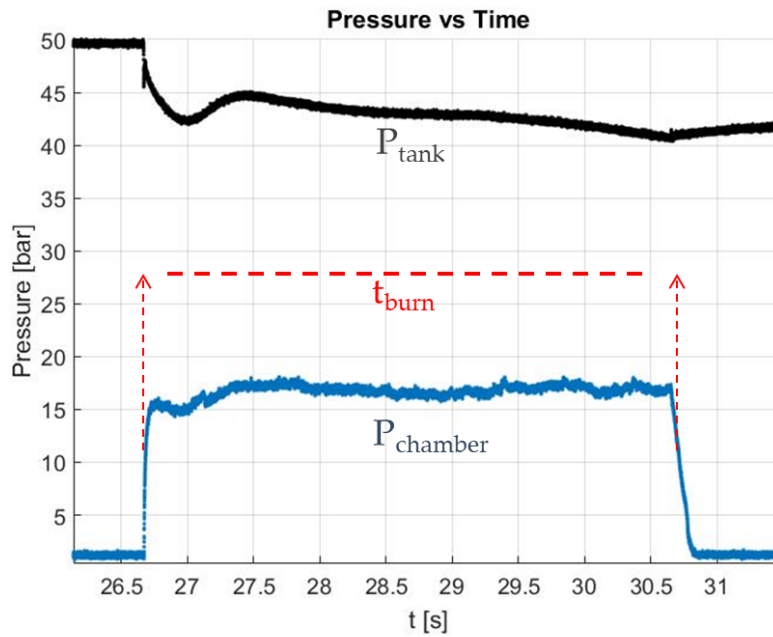


Figure 4.2 : Typical pressure trace for 3.1 cm hybrid rocket motor test firing. Absolute pressures are given.

Table 4.1 : Important performance parameter results for a typical 3.1 cm hybrid rocket motor firing test.

Parameters	Values	Parameters	Values
Regression Rate - rdot (mm/s)	1.422	SP-1 N2O Diff	-9.70%
mox_avg (g/s)	26.75	η_{c^*}	94.2%
mf_avg (g/s)	4.995	η_{nozzle}	98.0%
Mox (g)	107	Isp (s)	176.5
Mf (g)	19.98	Inj CD_avg	0.188
OF_avg	5.36	t_burn (s)	4
Pc_avg (bar)	16.69	deltaP_avg (bar)	26.18
Ptank_avg (bar)	42.87	Gox (kg/m ² -s)	103.2

The complete result of the concluded tests can be seen in Figure 4.3 to Figure 4.5. All of the specific fuel combinations' performance characteristics will be discussed after the figures. One important point is that since there is no thrust measurement in this system, I_{sp} results are found by assuming a constant nozzle efficiency for all of the tests which is %98. The equation for this calculation is given in Equation 4.4.

$$I_{sp_{calculated}} = c_{theoretical}^* CF_{theoretical} \eta_{nozzle} \eta_{c^*} / g \quad (4.4)$$

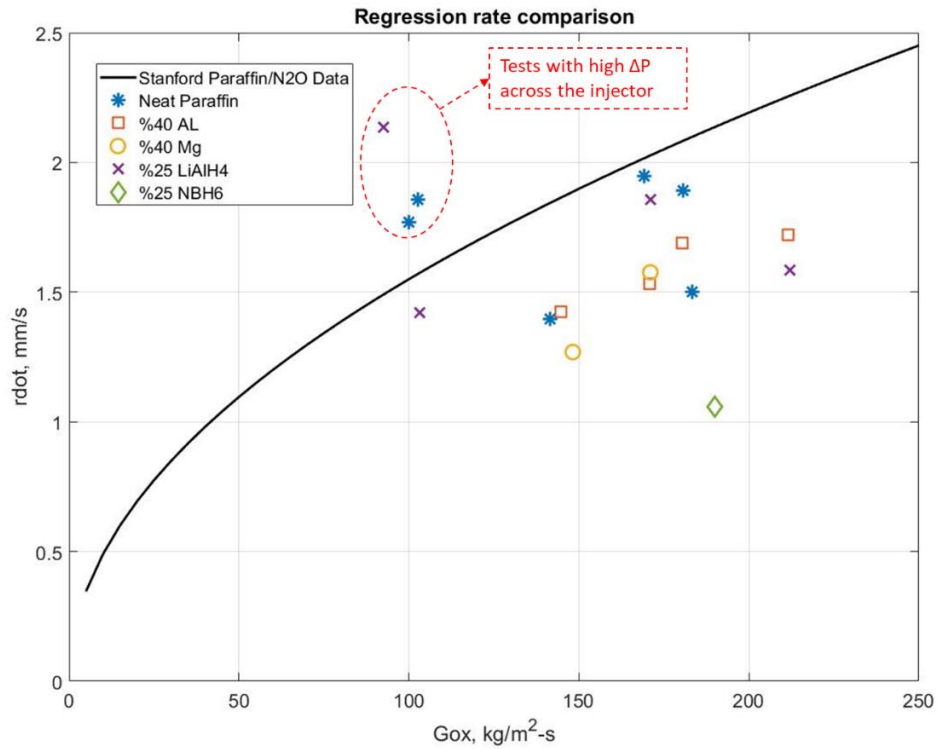


Figure 4.3 : Regression rate comparison of different kind of additives. Oxidizer is N_2O_L and fuel binder is paraffin.

4.1 Discussion of the Test Results

Before discussing each of the fuel configurations' performance results, there is an important point we want to talk about which is that the number of tests for each of these fuel configurations need to be increased. Since the cost of these materials are high, especially NBH_6 and $LiAlH_4$, the number of tests is limited.

If you look at Figure 4.3, there are 3 tests (one with $LiAlH_4$ and two with neat paraffin) that have high regression rate results. This increase in regression rate is believed to be happening because of the high ΔP across the injector which promotes the cavitation at

the injector, so the combustion is mainly with gaseous N_2O rather than the liquid N_2O . This difference in the oxidizer phase effects the combustion dynamic considerably which could be increasing the regression rate of the fuel and we believe the scatter of the neat paraffin-wax fuel regression rate data could be because of this phenomenon.

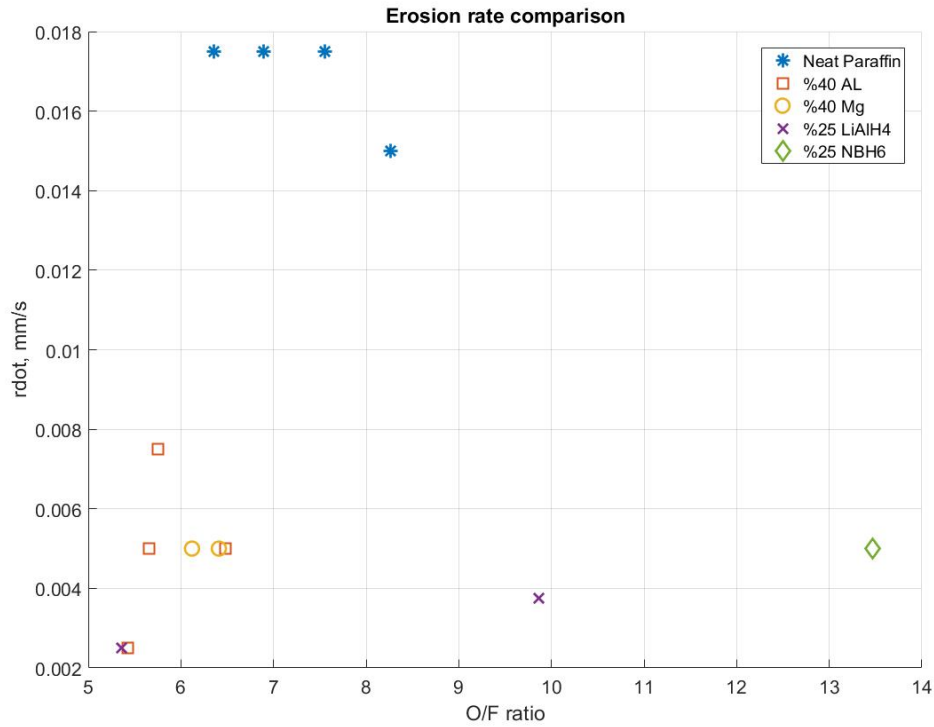


Figure 4.4 : Nozzle erosion rate comparison of different kind of additives. Oxidizer is N_2O_L and nozzle is graphite.

Neat Paraffin: It can be seen in Figure 4.3 that the neat paraffin case has lower regression rate values than SP-1 paraffin wax. SP-1 is a well-studied paraffin wax fuel in hybrid rocket motors by Karabeyoglu and its data can be found in literature [16]. The difference in neat paraffin regression rate results is because of the viscosity difference between the base fuel and SP-1. Other than this difference the neat paraffin case in this study has some scatter in the results. Since these tests are done with a blow-down N_2O_L , the conditions like liquid temperature, injector configuration and ignition process could affect the combustion process. Erosion rate for the neat paraffin case has nearly uniform value. Finally, the I_{sp} value of the neat paraffin case has one very low data which is thought as an outlier.

%40 Aluminum: Regression rate data for %40 AL case shows consistent increase with oxidizer mass flux. Other than the two neat paraffin case around $175 \text{ kg/m}^2\text{-s}$ oxidizer

mass flux, AL has increased the regression rate. Also, AL shows great improvement in nozzle erosion rate by reducing more than one third of neat paraffin case. Finally, AL experiment results shows a similar trend with theoretical results. Even though its optimum O/F ratio is around 4, it seems to increase the I_{sp} value of the neat paraffin around O/F ratio 6.

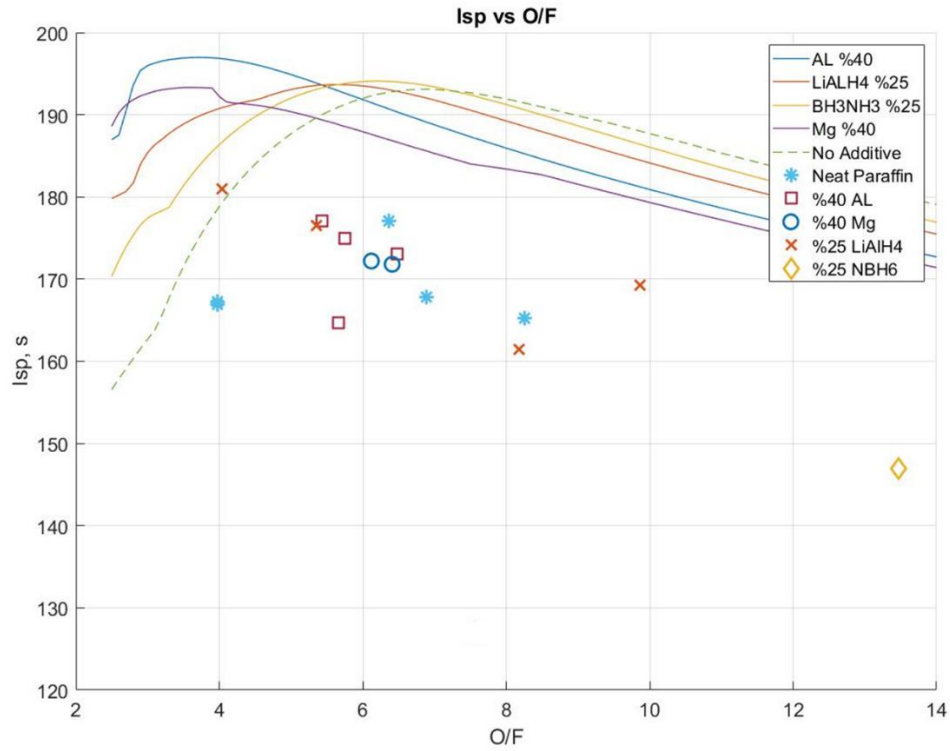


Figure 4.5 : I_{sp} comparison of different kind of additives. I_{sp} is calculated using Equation 4.3. Oxidizer is N_2O_L and fuel binder is paraffin wax.

%40 Magnesium: It is seen that regression and I_{sp} performance of %40 Mg fuel is lower than %40 AL fuel. This test result confirms the thermochemical calculations that Mg has lower gains than Al. Therefore, it is decided to focus more on AL in future studies.

%25 LiAlH₄: Lithium aluminum hydride is a good candidate for additive for hybrid rockets because of the hydrogen content which helps the I_{sp} performance and AL content which helps to reduce nozzle erosion rate. Also, LiAlH₄ is one of the most available and cost-effective metal hydrides. In this study LiAlH₄ is obtained from Merck. It is mixed with paraffin wax and spin casting method is employed in the production. Only two tests could be concluded. The regression rate of LiAlH₄ fuel in lower oxidizer mass flux shows good promise, but at the higher oxidizer mass flux AL

has higher regression rate. However, LiAlH_4 mass content is %25 in this study whereas Al has %40 mass ratio. Also, I_{sp} performance of %25 LiAlH_4 is nearly similar to %40 Al fuel with similar nozzle erosion rate reduction. These results show that LiAlH_4 is a very good candidate for future study with more tests and more mass ratio inside paraffin wax fuel.

%25 NBH_6 : Ammonia borane has received significant interest as a storage medium for hydrogen, especially fuel source for motor vehicles. It decomposes on heating which releases hydrogen. Also, ammonia borane is able to exist as a solid at room temperature and sea level pressure which makes it easily storable hydrogen source. Ammonia borane, which gives considerable amount of hydrogen when it decomposes, would be very suitable hybrid rocket fuel additive because hydrogen and oxygen reaction gives the highest heating value per unit mass and low molecular weight combustion products. In this study ammonia borane is obtained from a university lab in a very small quantity because of the cost of synthesizing of this material. A bigger batch of ammonia borane was not available. More than 3 other sources are searched, but none of them could supply this material. Only one hybrid rocket motor test firing was made with NBH_6 . In this test it is seen that the regression rate is considerably lower than neat paraffin. This low regression rate, also, resulted a high O/F ratio which made it harder to compare the other test results' I_{sp} with NBH_6 fuel test.

The conclusions of the N_2O_L tests are:

- Using performance enhancing additives to increase the regression rate of paraffin-based hybrid rocket fuel has no significant improvements. The regression rate results do not justify using these additives which are costly and make the production of fuel harder Figure 4.3.
- Aluminum is a good additive for N_2O_L systems. It increases the I_{sp} performance and reduces the optimum O/F ratio which in turn reduces the required volume for propellant. Also, it helps to reduce the nozzle erosion rate which is a crucial improvement in upper stage rocket motors Figure 4.5.
- Lithium aluminum hydride shows similar performance characteristics to aluminum, but its ratio in paraffin wax is %25 rather than %40 like in Al cases. This suggests that by increasing the LiAlH_4 mass ratio, performance can be increased

beyond Al fuel cases. However, one disadvantage of LiAlH_4 is the cost. Therefore, more small-scale tests should be done to better evaluate this additive performance.

- Magnesium addition does not show significant improvement, so in future studies it will not be in our focus.
- Ammonium borane could be a promising material for hybrid rocket fuel additive, but its cost, availability and problems when mixing with melted paraffin are needed to be resolved for future uses.





5. GASEOUS OXYGEN MOTOR TESTS and RESULTS

Even though there is a small I_{sp} increase with $LiAlH_4$ and NBH_6 , the materials are very expensive, not widely available and not easy to handle. Mg seems to be a good choice for nozzle erosion reduction, but its available energy per unit mass of propellant is lower than aluminum. There are other possible energetic materials that can be used for this study, but some of them are not considered because of toxicity (such as Be), some of them because of availability (such as AlH_3) and some of them because of ignition properties (such as B).

In the light of these information, we have decided that studying aluminum addition to hybrid rocket fuel would be the best choice. Aluminum addition reduces the graphite nozzle erosion rate considerably, increases the fuel density, decreases the optimum O/F ratio. Aluminum is, also, cost effective and widely available.

It is seen that the nozzle erosion rate reduction effect of aluminum addition is very substantial. Therefore, it is decided to focus on this characteristic and the remaining test plan changed accordingly.

Because of its more rigorous erosion potential, gaseous oxygen will be used as oxidizer rather than N_2O . If the erosion problem is mitigated with GOX, similar improvements are also expected for lower energy oxidizers used in hybrid systems, such as N_2O or H_2O_2 .

5.1 Hybrid Rocket Nozzle Erosion

As stated before, even though the liquefying solid fuels substantially increase the regression rates, there exist another important challenge that needs to be addressed in order to use hybrid motors for missions require long burn times such as in-space applications. This challenge is the high heat transfers and oxidation rates that the ablative nozzles suffer especially at the throat region, which could lead to severe erosion of the nozzle material. Sutton and Biblarz [1] divide the most common approaches to solving this problem in rocket motors to two main categories which are

“steady state” and “transient”. Regenerative cooling at the nozzle throat is the most viable method for steady state and ablative cooling is the most feasible method for transient. Since conventional hybrid rockets use liquid oxidizer, the regenerative cooling method must use the oxidizer as the cooling fluid. Even though it is a theoretical possibility, using an oxidizing agent as a coolant introduces major challenges and hazards. This type of industry-proven liquid oxidizer based regenerative cooling system is not currently available. Therefore, hybrid rocket developers commonly use the ablative cooling approach in the nozzle throat region [18], which introduces an erosion rate for the nozzle material. It is well known that the nozzle erosion rate is due to chemical (oxidizing) reactions and/or physical abrasion by condensed phase particles. In hybrid rockets it is believed that the main contribution to the erosion comes from the oxidizing reactions between the nozzle material and the oxidizing combustion products [19].

Carbon graphite nozzles are the most common type of ablative material used in hybrid rockets, which is also used extensively in solid rocket propulsion [1]. Thus, the extensive work on solid rocket nozzles can be used in hybrid rocket development. That being said, in hybrid rocket motors the concentration of the oxidizing agents in the combustion products is higher compared to solid rocket motors, potentially amplifying the severity of chemical nozzle erosion rate [20]. The average hybrid rocket nozzle erosion rate that we have seen in our studies are 0.02 mm/s for N_2O oxidizer and 0.1 mm/s for gaseous oxygen (GOX) oxidizer. The substantially higher nozzle erosion rate is expected for GOX because of the significantly higher combustion temperature.

The two primary effects of nozzle throat erosion on the I_{sp} performance are caused by the reduction in the nozzle area ratio and reduction in the chamber pressure (P_c) of the motor. The performance variation of a hybrid rocket with and without nozzle erosion has been estimated for a motor operating with parameters given in Table 5.1.

The hybrid rocket motor performance with the given parameters is calculated using Chemical Equilibrium Applications by NASA [17]. As initial conditions chamber pressure, nozzle throat diameter and fuel inner diameters are given. These parameters are then updated in every 0.01 s. Fuel regression rate calculation is shown in Equation 5.1. The constants are taken for paraffin-based fuel from reference 13. Nozzle throat area is calculated from the reference nozzle erosion rate given in Table 5.1. Chamber

pressure updated in each time step by using the calculated c^* from CEA, current nozzle throat area and total mass flow rate, Equation 5.2. I_{sp} is taken from CEA.

Table 5.1 : Hybrid rocket motor parameters for nozzle erosion effect study.

Parameter	Value
Average O/F ratio	2.6
Fuel outer diameter, cm	65
Fuel length, cm	150
Initial P_c , bar	25
Nozzle area ratio	70
Exit pressure, bar	0 (vacuum)
Reference nozzle erosion rate	0.09 mm/s
Oxidizer	Gaseous oxygen
Fuel	Paraffin-based

It can be seen in Figure 5.1 and Figure 5.2 that there is a considerable amount of erosion driven performance loss for an upper stage hybrid rocket motor burning for 3 minutes. The I_{sp} loss due to erosion is 6% and chamber pressure drops by 9.8 bar. This reduction in the chamber pressure could potentially affect the stability and efficiency of the motor. The expected performance improvement for 30% and 50% reduction in the linear erosion rate is also shown in Figure 5.1. 30% and 50% reduction in nozzle erosion generates I_{sp} increase of 0.8% and 1.67%, respectively.

$$\bar{r} = 0.117 \bar{G}_{ox}^{0.62} \quad (5.1)$$

$$P_c = \frac{c^* \dot{m}_{tot}}{A_{throat}} \quad (5.2)$$

The demonstrated high sensitivity of I_{sp} performance on nozzle erosion rate is the primary motivation of this study, which focuses on the use of metal powder additives in the hybrid fuel to address the nozzle erosion problem. It is well known that metal oxidizers, such as alumina (Al_2O_3), can absorb a significant fraction of oxygen, reducing the oxidizing species mol fraction at the nozzle throat and in turn reducing the nozzle erosion rate due to chemical oxidation.

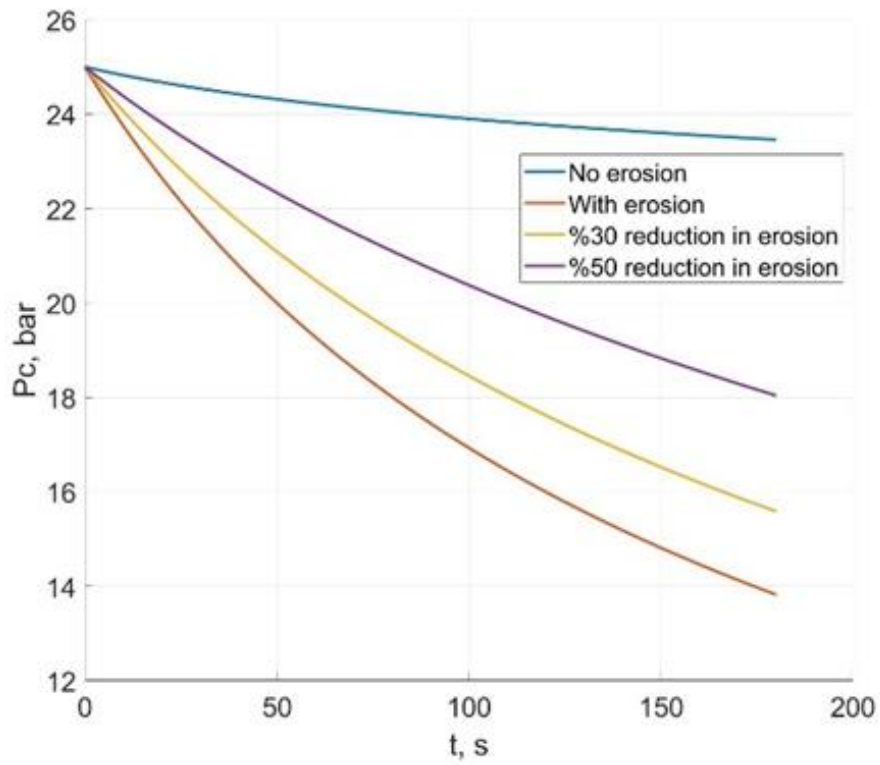


Figure 5.1 : Hybrid rocket motor performance with and without nozzle erosion. P_c time graph.

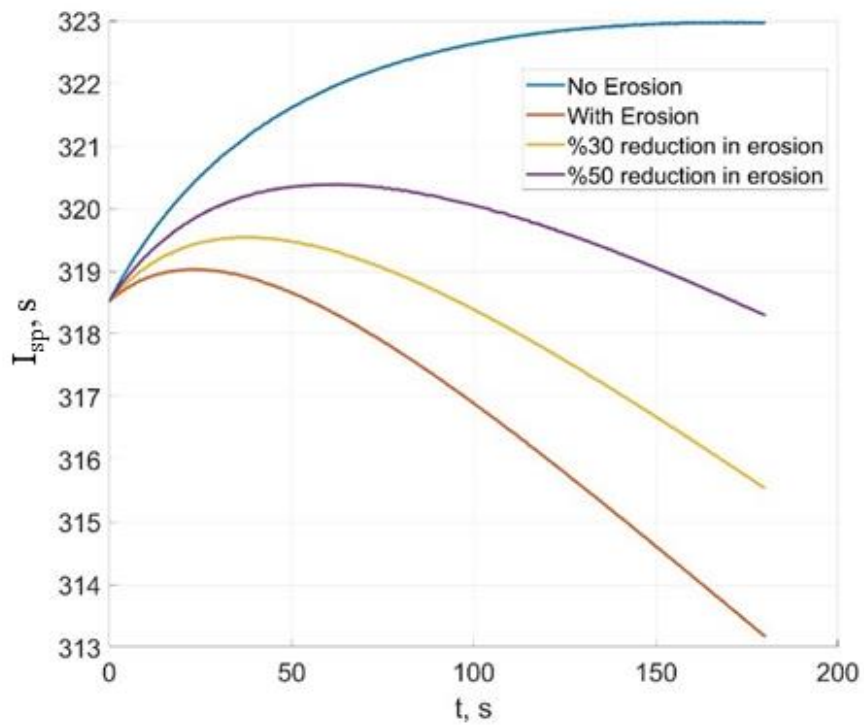


Figure 5.2 : Hybrid rocket motor performance with and without nozzle erosion. I_{sp} time graph.

5.2 Fuel Preparation with Highly Aluminized Ring

Paraffin wax ($C_{32}H_{66}$) is the main binder of the hybrid rocket solid fuel grain and 3-micron spherical shaped aluminum powder with 98.8% purity is the additive. It is decided to include the additives non-uniformly inside the fuel in order to simplify the fuel creation process. A fuel ring doped with high additive loadings is glued to the neat paraffin-based fuel. The length, additive ratio and the position of this ring are considered as free parameters. It is believed that this method can easily be scaled to larger hybrid rocket motors because the main fuel block containing no high-density powders can be spin casted and the short ring which contain energetic additives can be produced using layered casting techniques which eliminate the settling problem. This short ring is manufactured by adding the micro-aluminum powder to temperature-controlled liquid paraffin fuel and the cooled fuel is machined to the desired geometry. Hybrid rocket motor design can be seen Figure 5.3 and an example of this fuels can be seen in Figure 5.4. A 75% Al doped paraffin fuel ring is added to the front of the paraffin-based fuel. The length of this ring is 12 mm and this results in a total Al loading of 7% by mass in the entire fuel. The aluminum powder used in this research has a mean diameter of 3 micrometers (μm) and aluminum powder purity is 98.8%.

The total aluminum loading inside the fuel is chosen to be 7% because increasing this value decreases the theoretical I_{sp} with gaseous oxygen (dissociation effect). The maximum theoretical I_{sp} values for different AL loadings are given in Table 5.2 and I_{sp} vs O/F ratio graph for 7% AL loading is given in Figure 5.5. These calculations are done using CEA. Also, adding more aluminum to the fuel decreases nozzle efficiency because of the two-phase losses caused by condensed phase Al_2O_3 .

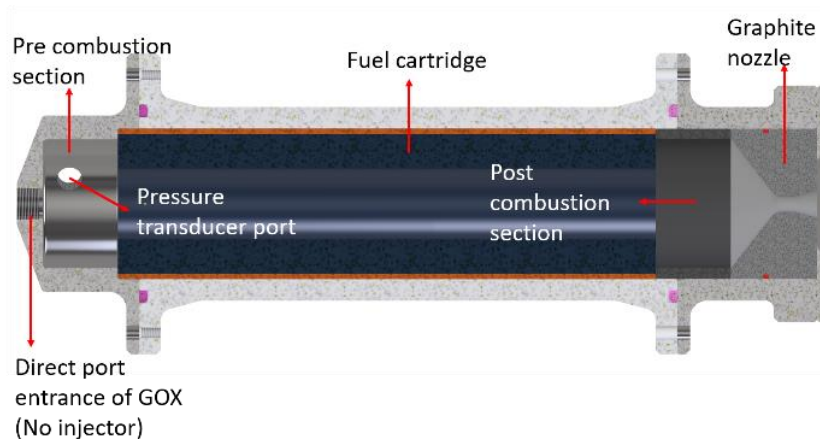


Figure 5.3 : Hybrid rocket motor design, 6.5 cm fuel outer diameter.



Figure 5.4 : Hybrid rocket fuels used in the tests: a) Aluminum added fuel ring and paraffin-based fuel, b) Al ring attached to the front of the paraffin-based fuel, c) Uniformly distributed Al fuels.

Table 5.2 : Maximum theoretical I_{sp} values of paraffin-based fuel with different AL loadings.

Fuel	Maximum Theoretical I_{sp} , s	Best I_{sp} O/F ratio
No additives	269.4	2.44
%7 Al addition	269.0	2.24
%20 Al addition	268.4	1.86
%40 Al addition	266.2	1.28
Oxidizer is GOX, AR is 6 and P_{amb} is 1 bar.		

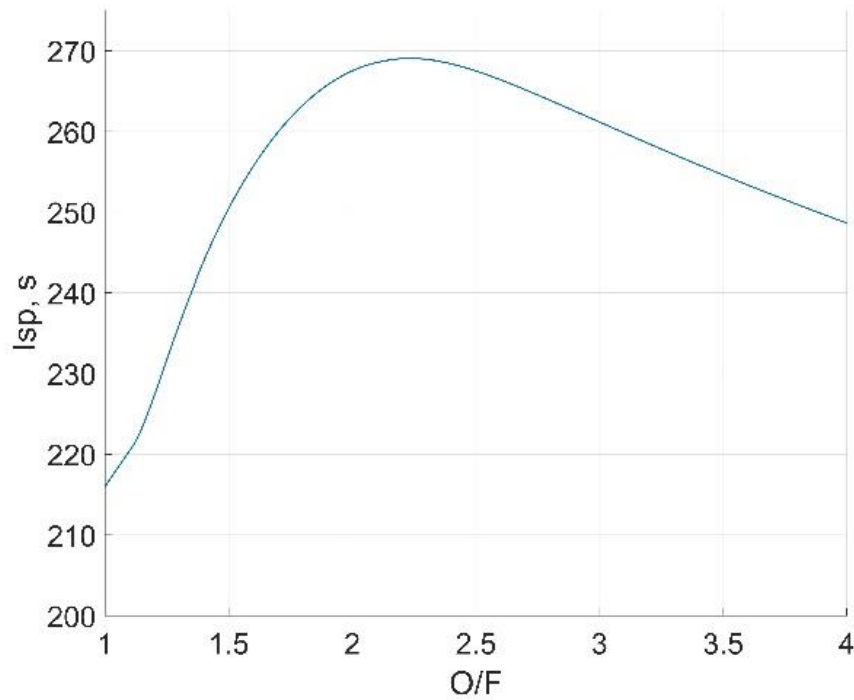


Figure 5.5 : I_{sp} vs O/F ratio for %7 Al loaded paraffin-based fuel. AR is 6 and P_{amb} is 1 bar.

5.3 Carbon-graphite Nozzle Design, Specifications and Measurement Technique

Properties of the carbon-graphite grade that is used in all test firings are listed in Table 5.3. Porosity, grain size, ash content, thermal conductivity and coefficient of thermal expansion play important role in selection of graphite type. For example, if graphite grade with high thermal conductivity is used, heat from the nozzle throat is transmitted to the outer surface more quickly which increases the erosion onset time. Grain size is an important parameter for nozzle erosion rate. Smaller grain size leads to lower porosity which in turn means reduced erosion rates as pointed out by Chelliah and Makino [18].

Table 5.3 : Detailed properties of the carbon-graphite grade.

Grain Size	Porosity	Ash Content	CTE	Thermal Conductivity	Density	Hardness – Rockwell H	Isotropy
8 μm	7%	300 ppm	6.0 $\times 10^{-6}/^{\circ}\text{C}$	105 W/ m°C	1.84 g/cm^3	<95	Isotropic Graphite

Throat diameter of the nozzle is measured before and after the tests to obtain the nozzle erosion rates. The measurements are done both by using calipers and image processing techniques. Photos of the nozzles are analyzed using Matlab software to determine the final diameter of the nozzle throat. Manual throat diameter measurements are used to check the results obtained from the image processing technique.

All carbon-graphite nozzles are machined using water injection to prevent dust formation. Even though better erosion results can be obtained when graphite is processed without water, practical limitations of the fabrication facility required wet machining.

Nozzle design can be seen in Figure 5.6, all dimensions are in mm. Nozzle area ratio is nearly 2.94.

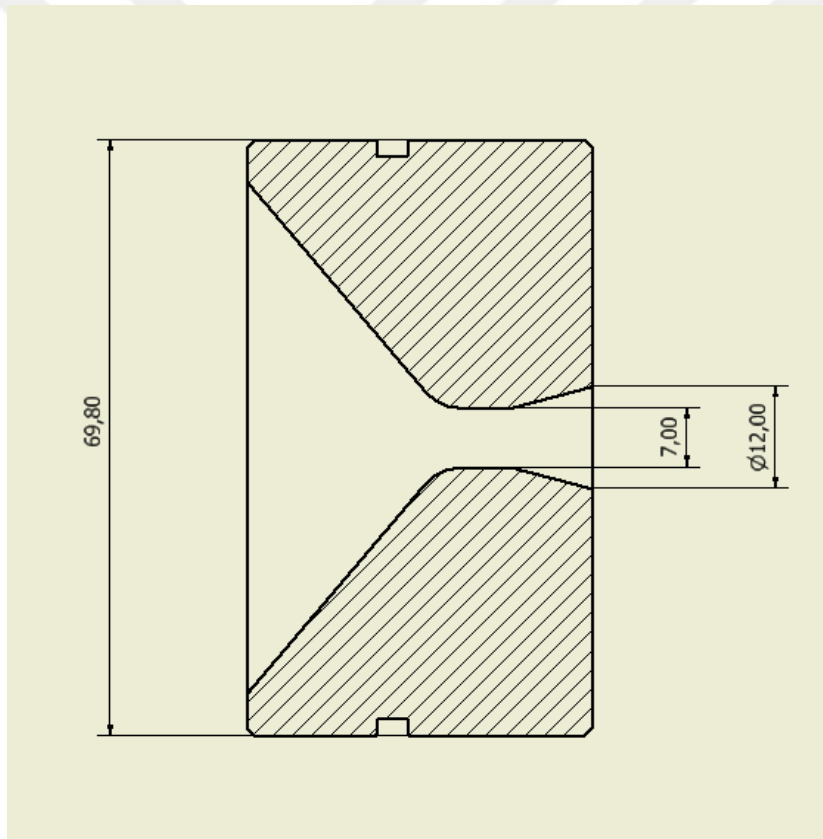


Figure 5.6 : Carbon-graphite nozzle design and dimensions.

5.4 Motor Hot Firing Tests and Discussions

Hybrid rocket motor hot firing tests are started with reference paraffin-based fuels without any additives and it continued with additive added fuel tests. A typical pressure time trace for 6.5 cm hybrid rocket motor test is given in Figure 5.7. As can be seen in

the Figure 5.7, there is a specific point in the ΔP ($P_{tank} - P_{chamber}$) time trace in which the ΔP increases. This point in time is the start of the nozzle throat erosion which we call it as erosion onset point.

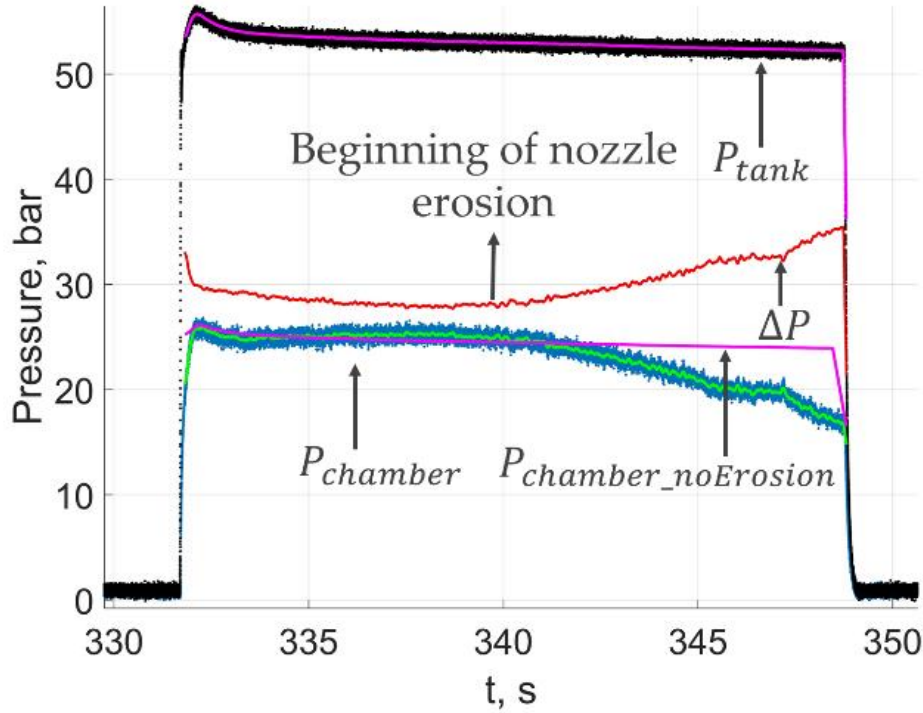


Figure 5.7 : Typical pressure time trace for 6.5 cm hybrid rocket motor test firing.

The time to the onset of the erosion can also be identified by examining the difference between the measured and theoretical chamber pressure curves. The theoretical chamber pressure calculation is based on Equation 5.1. The total mass flow rate is calculated based on choked orifice flow of GOX and measured fuel mass reduction during the test. Since the tank pressure is relatively constant, the change in oxidizer mass flow rate is under 1%. The c^* is calculated using CEA for the estimated O/F ratio during the motor test and its value changes from 1800 to 1770 m/s. The change in theoretical c^* is only 1.6% during the burn. The combustion efficiency, η_c , is assumed to be constant and its value is 95%. There might be a small change in the c^* efficiency during the burn, but its effect on the final result is believed to be small. Under these assumptions (with zero erosion rate) it can be seen in Figure 5.7 that the total change in theoretical chamber pressure is under 2 bar. Therefore, the difference between the measured and theoretical chamber pressure comes from the nozzle throat area increase and the point of divergence is the nozzle erosion onset time.

$$P_{c_theoretical} = \frac{\dot{m} c^* \eta_c}{A_{throat}} \quad (5.2)$$

The onset time of the erosion is included in the nozzle erosion rate calculation. Since the graphite material of the nozzle needs to be heated to a certain temperature before the erosion starts, the onset time is subtracted from the burn time. Measured nozzle diameter increase and the effective erosion time is used to get the nozzle erosion rate, Equation 5.2. Nozzle erosion onset time is an important parameter in itself. If the onset time is long enough, for short burn time motors, erosion can be fully avoided.

$$\bar{r}_n = \frac{D_{t_f} - D_{t_i}}{2(t_{burn} - t_{erosion\ onset})} \quad (5.2)$$

The average linear regression rate and average oxidizer mass flux were calculated using Equation 5.3 and Equation 5.4. The arithmetic average of the initial and final port diameters is used in the average oxidizer mass flux calculation which is shown to have lowest level of error [16]. Also, as pointed out earlier, the detailed relative error analysis is given in Appendix A.

$$\bar{r} = \frac{D_i - D_f}{2t_b} \quad (5.3)$$

$$\bar{G}_o = \frac{16\dot{m}_o}{\pi(D_i + D_f)^2} \quad (5.4)$$

An example motor hot firing test can be seen in Figure 5.8 and its pressure time trace is shown in Figure 5.7. The motor burn is healthy and stable. Also, its O/F ratio is close to optimum c^* O/F ratio which is 2.18.

5.4.1 Fuel Regression Rate Results

Even though it is not the focus of this chapter, fuel regression rate data for the paraffin-based fuel, DY-12, is reported in this section, as can be seen in Figure 5.9. The regression rate results for the uniform aluminum addition to the paraffin-based fuel and the case of heavily loaded ring concept (at different positions - at the front and end of the fuel) are given.

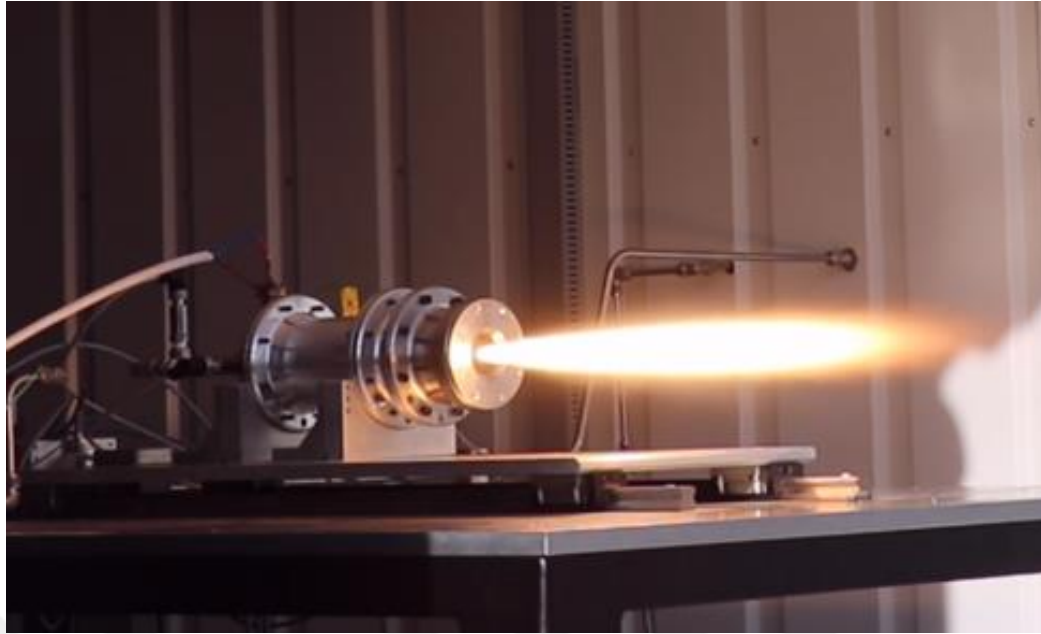


Figure 5.8 : An example motor hot firing test with GOX oxidizer and 6.5 cm outer diameter fuel.

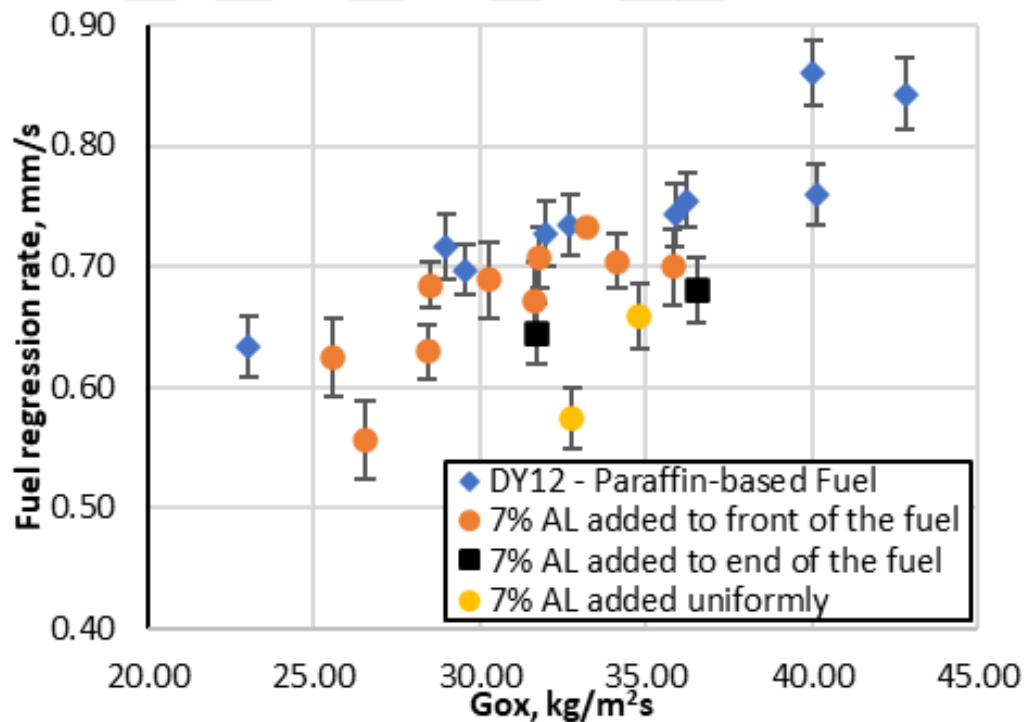


Figure 5.9 : Regression rate comparison of different kind of fuels. Oxidizer is GOX.

It can be seen that the regression rate for the aluminum ring added to the front of the DY12 fuel is nearly the same as the regression rate of the paraffin-based DY12 fuel at high oxidizer fluxes. It is slightly lower at low fluxes. There was a small diameter difference between the AL-ring section and the rest of the fuel surface after the test,

indicating a slight difference in the regression rate. The fuel cross section after the test can be seen in Figure 5.10. It is expected to have a larger local regression rate difference for the two fuel formulations because of the lower viscosity of the neat fuel [21]. However, post-test examination has shown only a slight diameter difference and this is attributed to the increase in local mixing created by the forward and backward steps formed during the burning process. The increase in the local heat transfer prevents the formation of a large difference in the fuel diameters.

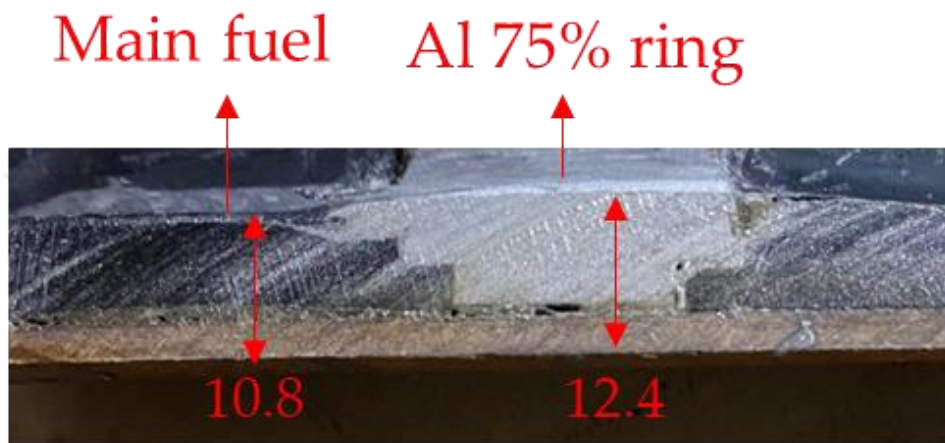


Figure 5.10 : Fuel cross section after the test. Dimensions are in mm.

It is seen that, for 6.5 cm fuel outer diameter hybrid rocket motor and at our operating conditions, addition of micro aluminum to the fuel as a ring has relatively low impact on the regression rate. A regression rate decrease is seen for the uniformly distributed AL fuel, most likely caused by an increase in the melt layer viscosity due to aluminum powder addition.

5.4.2 Nozzle Erosion Rate and Onset Results

The graphite nozzle erosion rate and onset time results can be seen in Figure 5.11 and Figure 5.12. It should be noted that, because each of the reported tests have different chamber pressures, the nozzle erosion rate results are corrected for chamber pressure to better compare the results. This correction equation used a linear dependence on the chamber pressure because in Equation 5.5 “m” value is generally 1 [16]. Pressure correction took 25 bar as reference pressure. a_n , is an empirical rate constant for nozzle erosion.

$$\bar{r}_n = a_n \left(\frac{C_d}{c_{theo}^* \eta} \right)^m P_c^m \quad (5.5)$$

$$\bar{r}_{n \text{ corrected}} = \bar{r}_n \frac{P_{cref}}{P_c} \quad (5.6)$$

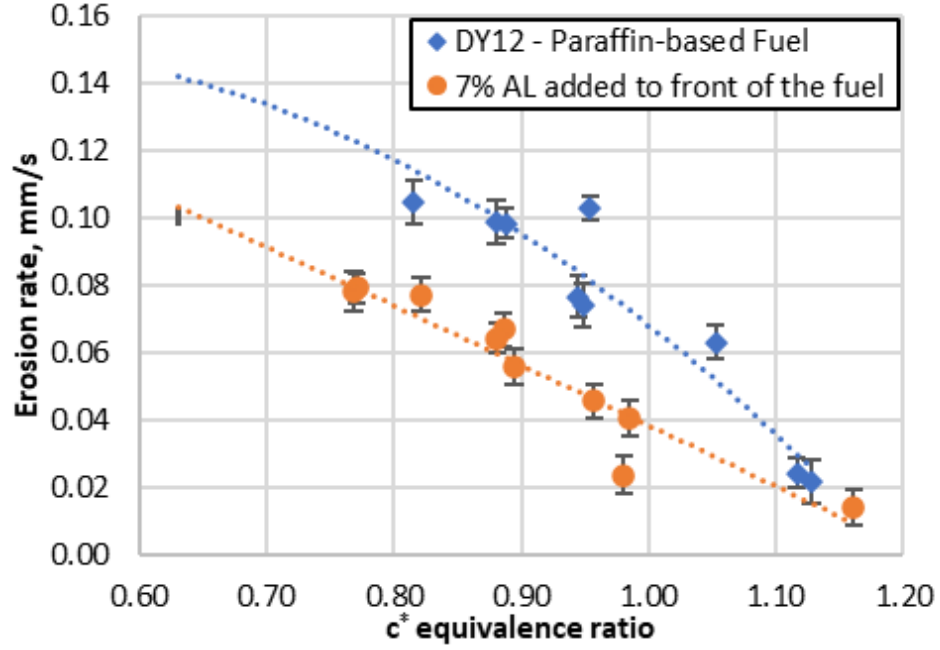


Figure 5.11 : Nozzle throat erosion rate comparison vs ϕ ratio. The nozzle material is carbon-graphite.

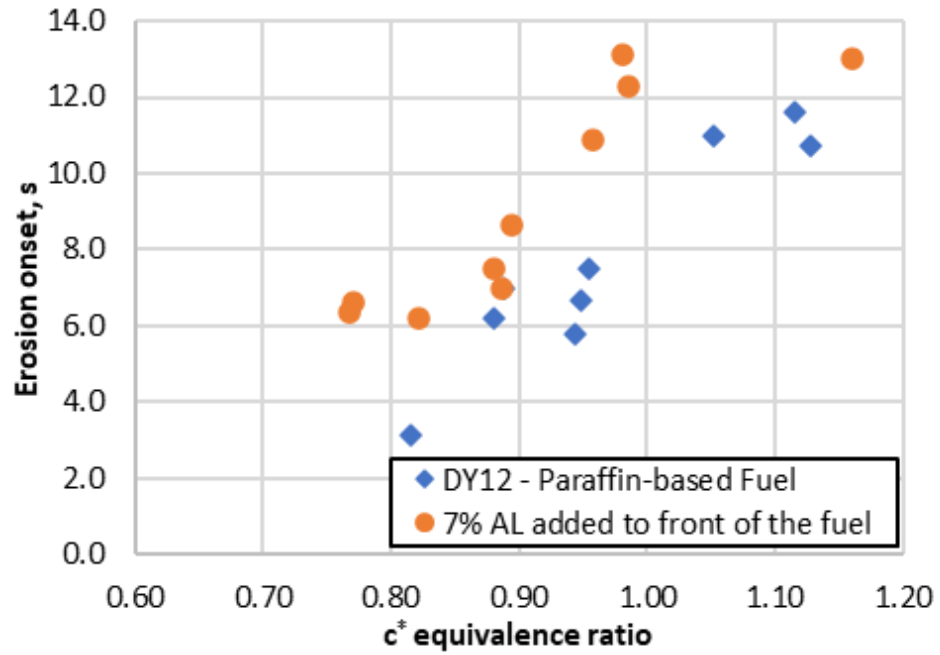


Figure 5.12 : Nozzle throat erosion onset comparison vs ϕ ratio.

In addition to the pressure correction, the right way to compare the different fuel's nozzle erosion results is to use the c^* equivalence ratio (ϕ) because the main focus is the hybrid rocket motor performance. If this ratio is 1, it means the best c^* O/F ratio is achieved. Bigger than 1 is fuel rich condition and lower than 1 is fuel lean condition. The definition of O/F and c^* equivalence ratio is given in Equation 5.7 and Equation 5.8. Optimum c^* O/F ratio for DY12 fuel is 2.21 and 7% Al added fuel is 2.02.

$$O/F = \frac{\dot{m}_{oxidizer}}{\dot{m}_{fuel}} \quad (5.7)$$

$$\phi = c^* \text{ equivalence ratio} = \frac{O/F_{@optimum c^*}}{O/F} \quad (5.8)$$

It can be seen in Figure 5.11 and Figure 5.12 that aluminum ring added to the front of the DY12 fuel increased the erosion onset time and decreased the nozzle erosion rate. Nozzle erosion rate reduction at equivalence ratio of 0.98 is nearly 42% and erosion onset time increase is close to 2 seconds. These effects decrease the total nozzle erosion to a great extent leading to an increase in motor performance.

The method of introducing the micro-aluminum addition to the paraffin-based fuel did not alter the performance characteristics drastically. As can be seen in Figure 5.13, adding the micro-aluminum ring to the front or to the after of the fuel, as well as, distributing the aluminum uniformly inside the fuel had a similar effect. This result gives us confidence to continue working with the aluminum ring addition technique because this method would allow for spin casting of hybrid fuels at larger diameters.

In addition to the axial location of the Al rich fuel ring, we have also investigated the effect of Al mass ratio on the erosion rate. The nozzle erosion rate results of these tests can be seen in Figure 5.13. Even though 7% Al addition by mass decreased the nozzle erosion rate considerably, 14% Al addition had a small effect (compared to the neat fuel case). Therefore, it is thought that there would be an optimum Al mass ratio that maximizes the nozzle erosion rate reduction. In order to better understand this characteristic, two other Al mass ratio tests at equivalence ratio of 0.76 are completed. The detailed nozzle erosion rate values at equivalence ratio of 0.76 can be seen in Table 5.4.

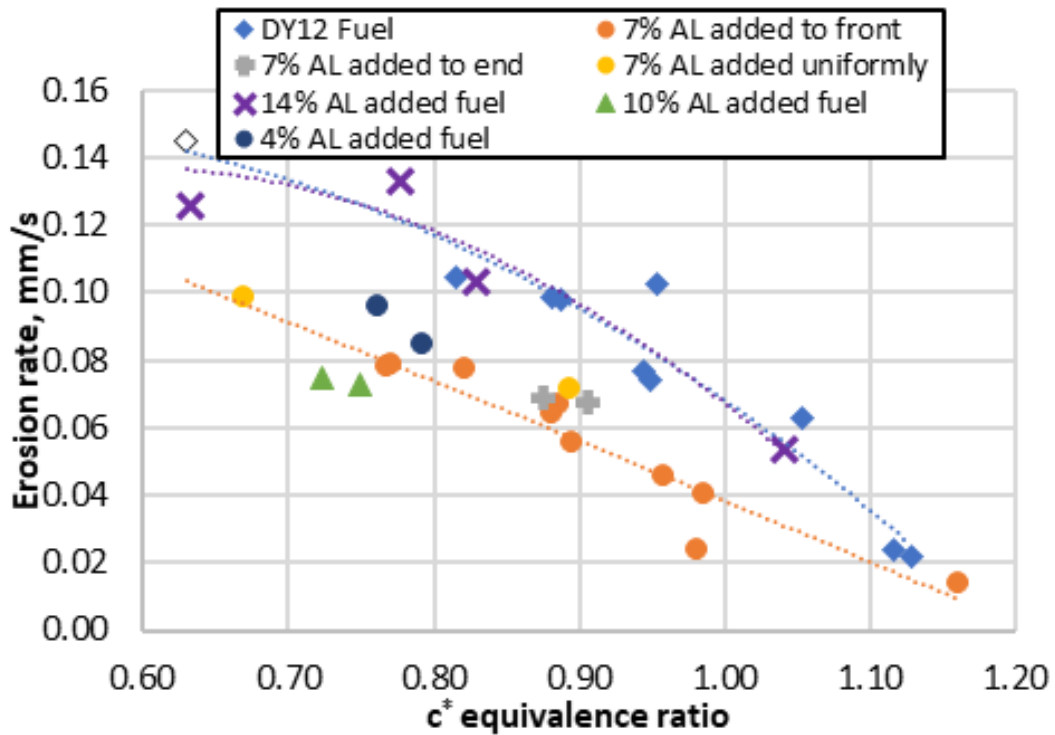


Figure 5.13 : The effects of different AL mass addition to the nozzle throat erosion rate.

Table 5.4 : Detailed throat erosion rate values at 25 bar chamber pressure.

Test #	Al % ratio	Ø	Erosion rate, mm/s
Interpolated	No Al	0.76	0.1225
ECT 45	4% Al	0.77	0.0998
ECT 11	7% Al	0.77	0.0783
ECT 33	10% Al	0.76	0.0744
Interpolated	14% Al	0.76	0.125

The results resented in Table 5.4 show that the erosion rate reduction generated by the addition of micron size aluminum powder has an optimum concentration. This optimum concentration that leads to minimum erosion rate is around 10% Al by mass. The detailed results of the conducted tests are given in the next chapter.

This nozzle erosion reduction achieved by micro-aluminum addition is believed to be caused by two mechanisms. The first one is the creation of a liquid Al_2O_3 film on the surface of nozzle throat. Since the boiling temperature of Al_2O_3 is 3250 K, this material is mostly in the liquid phase at the throat. The Al_2O_3 liquid fuel film protects the graphite surface from the oxidizing agents such as O_2 , O , H_2O , CO_2 and decreases the

nozzle erosion. The second mechanism is the reduction of the oxidizing species at the nozzle throat, which will be studied more thoroughly in the next section. Also, all of the motor test data for gaseous oxygen oxidizer system is given in the next section in Table 5.5.



5.4.3 Gaseous Oxygen Motor Test Data

Table 5.5 : Gaseous oxygen motor test data

Test#	m_{fuel} , g	m_{fuel} final, g	η_c , %	D_b , mm	D_t final, mm	t_{burn} , s	P_c , bar	rdot , mm/s	m_{ox} , g/s	G_{ox} , kg/m ² .s	O/F ratio	$\emptyset$	Erosion Onset, s	Erosion rate, mm/s	Erosion rate (corrected for P_c)
DY12 Paraffin-Based Fuel - No additives															
ECT01	424.8	293.1	87	7.51	7.52	7.92	20.37	0.734	40.67	32.72	2.45	0.90	8.0	No erosion	No erosion
ECT02	436.9	100.8	87.1	7.51	9.35	19.94	18.00	0.633	39.05	23.05	2.32	0.95	7.5	0.0740	0.1028
ECT03	669.1	316.1	92	7.95	8.00	11.70	30.20	0.843	59.00	42.80	1.96	1.13	10.8	0.0263	0.0218
ECT04	660.2	177.1	92.4	7.53	7.85	16.79	32.00	0.755	56.86	36.26	1.98	1.12	11.6	0.0308	0.0241
ECT05	407.8	190.5	90.8	7.50	8.55	11.64	23.28	0.717	46.90	29.00	2.51	0.88	6.2	0.0920	0.0988
ECT06	552.1	214.6	90.9	7.50	8.00	14.86	25.86	0.727	47.75	32.00	2.10	1.05	11.0	0.0650	0.0628
ECT07	457.0	157.3	89.6	6.98	8.80	16.98	23.18	0.697	44.00	29.56	2.49	0.89	7.0	0.0910	0.0981
ECT09	519.6	224.2	90.9	7.47	8.36	11.58	30.67	0.861	59.45	40.04	2.33	0.95	6.7	0.0910	0.0742
ECT20	578.1	307.1	89.7	7.50	8.49	11.90	26.47	0.759	53.31	40.13	2.34	0.94	5.8	0.0811	0.0766
ECT25	443.5	231.8	89	7.48	9.00	11.60	21.50	0.743	49.51	35.88	2.71	0.82	3.2	0.0900	0.1047
7% AL (by mass) added Fuel - AL ring added to the front of the fuel															
ECT08	476.5	209.7	87	7.05	8.00	14.86	22.54	0.684	41.00	28.53	2.28	0.89	7.0	0.0602	0.0668
ECT10	470.6	196.2	89.8	6.97	8.30	14.85	24.93	0.689	45.45	30.28	2.46	0.82	6.2	0.0769	0.0771
ECT11	428.3	212.1	93.4	6.96	7.98	12.86	25.00	0.629	44.28	28.44	2.63	0.77	6.4	0.0783	0.0783
ECT14	708.6	340.5	94.3	7.95	7.98	13.71	25.27	0.704	46.62	34.13	1.74	1.16	13.0	0.0141	0.0139

Table 5.5 (continued): Gaseous oxygen motor test data

Test#	$m_{\text{fuel, g}}$	$m_{\text{fuel, final, g}}$	$\eta_c, \%$	D_b, mm	$D_t, \text{final, mm}$	$t_{\text{burn, s}}$	P_c, bar	rdot, mm/s	$m_{\text{ox, g/s}}$	$G_{\text{ox, kg/m}^2\text{s}}$	O/F ratio	$\emptyset$	Erosion Onset, s	Erosion rate, mm/s	Erosion rate (corrected for P_c)
ECT15	467.7	212.5	93	7.00	8.40	17.84	19.75	0.556	37.50	26.56	2.62	0.77	6.6	0.0624	0.0790
ECT21	587.2	283.3	93.8	7.50	8.13	13.88	26.72	0.700	49.46	35.81	2.26	0.89	8.6	0.0596	0.0558
7% AL (by mass) added Fuel - AL ring added to the end of the fuel															
ECT22	587.1	293.2	93	7.50	8.42	13.80	25.42	0.681	49.18	36.53	2.31	0.87	7.3	0.0703	0.0691
ECT23	557.4	244.0	93.8	7.54	8.43	14.82	24.78	0.644	47.21	31.73	2.23	0.91	8.2	0.0672	0.0678
7% AL (by mass) added Fuel - AL distributed uniformly inside the fuel															
ECT18	595.9	306.0	94.8	7.50	8.51	13.83	24.05	0.659	47.35	34.82	2.26	0.89	6.5	0.0686	0.0713
ECT19	475.4	267.3	95.2	7.00	9.09	14.85	20.24	0.575	42.37	32.79	3.02	0.67	1.8	0.0798	0.0986
14% AL (by mass) added Fuel - AL ring added to the front of the fuel															
ECT16	492.0	261.1	93.3	7.00	8.94	16.89	19.67	0.500	39.83	28.10	2.91	0.63	7.1	0.0990	0.1258
ECT17	593.0	298.7	91.7	7.45	8.77	13.69	25.00	0.616	50.92	34.00	2.37	0.78	8.7	0.1330	0.1330
ECT27	617.5	230.2	94.7	7.50	7.80	14.52	27.11	0.770	46.30	30.46	1.74	1.06	12.0	0.0600	0.0553
ECT29	449.7	159.1	97	7.02	8.63	13.66	25.48	0.730	46.40	27.62	2.18	0.84	6.3	0.1090	0.1069
10% AL (by mass) added Fuel - AL ring added to the front of the fuel															
ECT32	474.0	255.3	96.4	7.05	7.67	13.89	23.77	0.632	42.40	32.36	2.69	0.74	9.7	0.0736	0.0774
ECT33	462.7	231.2	93.8	7.05	7.90	13.90	23.78	0.633	43.29	30.06	2.60	0.76	7.9	0.0708	0.0744
4% AL (by mass) added Fuel - AL ring added to the front of the fuel															
ECT34	450.1	218.2	96.1	7.04	8.39	13.93	24.14	0.6797	45.07	33.29	2.71	0.77	6.93	0.0964	0.0998
ECT35	468.4	243.1	96.4	7.05	7.85	13.86	24.14	0.6603	42.19	31.66	2.6	0.81	8.92	0.084	0.0870

6. DISCUSSION OF NOZZLE EROSION TEST RESULTS

The main objective of this study is to present the experimental results of the AL loaded fuel ring and to show its effectiveness in reducing the nozzle erosion rate. Even though the potential mechanisms for the observed characteristics are also considered here briefly, the main focus of this study is to obtain accurate motor test data based under highly controlled testing environment.

The nozzle erosion in hybrid rocket motors is predominantly controlled by heterogeneous chemical reactions because the mechanical erosion causing condensed phase products at the chamber exit is very low compared to a solid rocket motor. The major oxidizing species at the nozzle entrance are CO_2 , H_2O , O , OH and O_2 . These species have to diffuse into the carbon-graphite nozzle surface and then depending on the wall temperature, the nozzle surface will be eroded by chemical oxidation.

6.1 Nozzle Erosion Theoretical Modeling

The theoretical approach to carbon-graphite nozzle erosion is described in Figure 6.1.

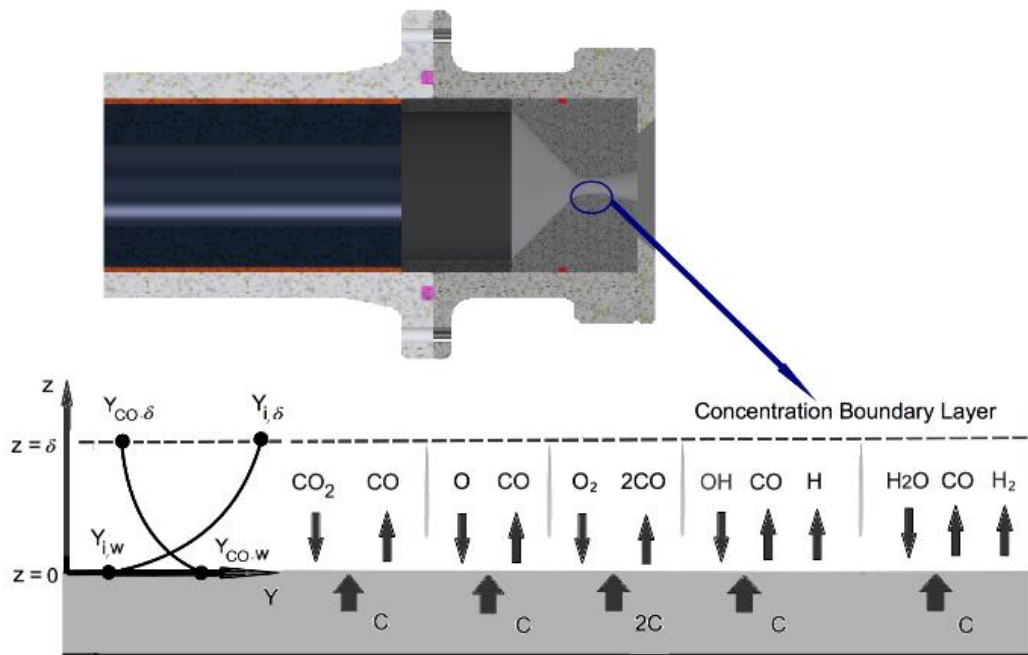


Figure 6.1 : Theoretical thermochemical nozzle erosion rate calculation approach.

The goal of this thesis is to identify the differences in the nozzle oxidation process between a micro-aluminum added and neat paraffin-based fuel hybrid rocket motor. There are some shortcomings of this method because of the assumptions for the underlying physics, but it will give a qualitative understanding of the nozzle erosion rate. There are three unknowns for the nozzle erosion rate solution, which are species mass fractions at the wall, wall temperature and erosion rate. These are solved by implementing a similar method to one film model solution for the carbon combustion [22] and using the diffusion boundary layer approach by Kamps et al [23]. This approach assumes that only diffusion of a single oxidizing species “i” in the negative z-direction (towards the surface) and CO in the positive z-direction are considered and the solution for surface erosion mass flux can be determined by the Equation 6.1. The derivation of this equation is given in [24].

$$\rho_n \dot{r}_i = \frac{(\rho D_{CO,i})_w}{\delta_i} \ln \left(\frac{1 + \frac{Y_{i,\delta}}{\xi_j}}{1 + \frac{Y_{i,w}}{\xi_j}} \right) \quad (6.1)$$

Where ρ , kg/m³ is density, D , m²/s is diffusivity and δ , m is boundary layer thickness for the diffusion. ξ is the stoichiometric mass ratio for each reaction. “i” is gas phase oxidizing species and “j” is each oxidizing reaction. The binary diffusion coefficient of CO is predicted from the Chapman-Enskog theory [22]. In this theory binary diffusion constant of arbitrary gases is given in Equation 6.2, where Ω and T^* given in Equation 6.3 and Equation 6.4.

$$D_{A,B} = \frac{0.0752 T^{3/2}}{P \Omega (\sigma_A + \sigma_B)^2} \sqrt{\frac{1}{MW_A} + \frac{1}{MW_B}} \quad (6.2)$$

$$\Omega = \frac{1.06036}{(T^*)^{0.15610}} + \frac{0.19300}{\exp(0.47635 T^*)} + \frac{1.03587}{\exp(1.52996 T^*)} + \frac{1.76474}{\exp(3.89411 T^*)} \quad (6.3)$$

$$T^* = \frac{T}{\sqrt{\Lambda_A \Lambda_B}} \quad (6.4)$$

The Lennard-Jones parameters for diffusion coefficient calculation is given in Table 6.1 for each species [22].

Table 6.1 : The Lennard-Jones parameters for diffusion coefficient [22].

Species	$\sigma_i, \text{\AA}$	Λ_i, K
CO	3.690	91.7
O	3.050	106.7
OH	3.147	79.8
O_2	3.467	106.7
H_2O	2.641	809.1
CO_2	3.941	195.2

Only parameter that needs to be determined for the binary diffusion calculation is the concentration boundary layer thickness. This is estimated from the equation by Gilliland-Sherwood [25]. Although, this equation is for diffusion of vapors into air streams in pipe flow, it is assumed that it will give a reasonable approximation the nozzle case.

$$\delta_i = \frac{d}{0.023Re^{0.83}Sc_i^{0.44}} \quad (6.5)$$

Reynold's number, Re , and Schmidt number, Sc_i , for each oxidizing species is calculated from the bulk flow.

$$Re = \frac{d\rho\sqrt{YRT}}{\mu}, \quad Sc_i = \frac{\mu}{(\rho D_{CO,i})_w} \quad (6.6)$$

The oxidizing species that diffused into the nozzle wall surface will react with the carbon-graphite according to Equation 6.7 and Equation 6.8:

$$\rho_n \dot{r}_i = k_j p_i^{n_j} \quad (6.7)$$

$$k_j(T_w) = A_j T_w^{b_j} \exp\left(\frac{-E_j}{R_u T_w}\right) \quad (6.8)$$

where, “ j ” is chemical reaction order and A_j , E_j , b_j are empirical rate constants.

Only the molecular oxygen has a different kinetic expression by Nagle and Stricland-Constable because it cannot be properly expressed by the Arrhenius equation given in Equation 6.7. In these equations p_i is the partial pressure of each oxidizing species (in atm).

The sum of each oxidizing species reactions will give the total erosion mass flux. The empirical heterogeneous rate constants and reaction order with carbon graphite is given in Table 6.2. These empirical constants are taken from Bradley et. al. [26] and their shortcomings are the temperature range of each reaction. As can be seen in Table 6.2 that, especially OH reaction, have low temperature range than expected nozzle flow conditions. However, as stated before, the focus in this study is to compare different fuel composition effects to the nozzle erosion. Therefore, these constants' accuracies are deemed suitable for our analysis.

Table 6.2 : Heterogenous chemical reaction rate constants with carbon-graphite.

Reaction	j	ξ_j	A_j	$\frac{E_j}{R_u}, K$	b_j	n_j	Temperature Range, K
$C_s + H_2O \rightarrow CO + H_2$	1	3.67	480,000	34,640	0.0	0.5	800-2500
$C_s + CO_2 \rightarrow 2CO$	2	1.50	9,000	34,280	0.0	0.5	800-2500
$C_s + OH \rightarrow CO + H$	3	1.42	361	0.0	-0.5	1.0	1575-1685
$C_s + O \rightarrow CO$	4	1.33	665.5	0.0	-0.5	1.0	1100-2100
$C_s + \frac{1}{2} O_2 \rightarrow CO$	5a	1.33	2,400	15,107	0.0	0.0	1273-2273
	5b		21.3	-2,065	0.0	0.0	
	5c		0.0535	7655	0.0	0.0	
	5d		18,100,000	48,845	0.0	0.0	

The core nozzle throat flow gas properties can be estimated using NASA CEA [17], assuming equilibrium flow conditions in the hybrid rocket motor. With the use of Equation 6.9 and Equation 6.10, species mass fractions' at the wall can be solved and erosion rate contribution for each separate oxidizing species can be calculated, assuming that the wall temperature is known either by estimating a wall temperature or solving the surface energy balance equation. The latter approach is used in this study and its details are given below.

$$\rho_n k_j \left(\frac{MW_{mix}}{MW_i} P Y_{i,w} \right)^n = \frac{(\rho D_{CO,i})_w}{\delta_i} \ln \left(\frac{1 + \frac{Y_{i,\delta}}{\xi_j}}{1 + \frac{Y_{i,w}}{\xi_j}} \right) \quad \text{for } j: 1 \text{ to } 4 \quad (6.9)$$

$$\rho_n \left(\left(\frac{k_{5a} P_{O_2} Z_w}{1 + k_{5b} Z_w} \right) + k_{5c} P_{O_2} (1 - Z_w) \right) = \frac{(\rho D_{CO, O_2})_w}{\delta_{O_2}} \ln \left(\frac{1 + \frac{Y_{O_2, \delta}}{\xi_5}}{1 + \frac{Y_{O_2, w}}{\xi_5}} \right) \quad \text{for } j: 5 \quad (6.10)$$

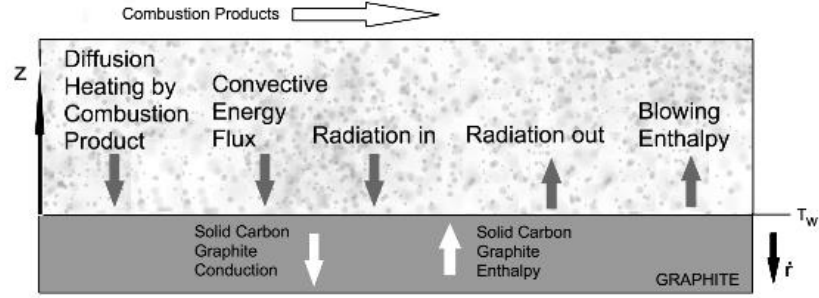


Figure 6.2 : Surface energy balance for ablating carbon-graphite nozzle material.

As stated before, there is another unknown for these calculations, which is the wall temperature T_w . To solve the wall temperature, surface mass and energy balance equations will be used, Equation 6.11 and Equation 6.12. This method is similar to the technique used by Bianchi and Nasuti [27] for calculating the thermochemical nozzle erosion in hybrid rocket motors.

$$(\rho v)_w = \dot{m} = \rho_s \dot{r} \quad (6.11)$$

$$\begin{aligned} k \frac{\partial T}{\partial z} |_w + \sum_{i=1}^N h_{i_w} \rho D_{im} \frac{\partial y_i}{\partial z} |_w + \dot{m} h_s + q_{rad_{in}} \\ = -k_s \frac{\partial T}{\partial z} |_s + q_{rad_{out}} + (\rho v)_w h_w \end{aligned} \quad (6.12)$$

Surface mass balance is multiplied with enthalpy and summed over all the species. Then it is substituted into the surface energy balance equation, which yields a compact equation for the surface energy balance. “w”, indices refer to wall and “s” indices refers to solid nozzle material.

$$\underbrace{k \frac{\partial T}{\partial z} |_w}_{\text{Convection}} + \underbrace{q_{rad_{in}}}_{\text{Radiation in}} = \underbrace{\sum_{i=1}^N \dot{m} h_{i_w}}_{\text{Ablation}} - \underbrace{q_{rad_{out}}}_{\text{Radiation out}} - \underbrace{k_s \frac{\partial T_s}{\partial z} |_s}_{\text{Solid Conduction}} \quad (6.13)$$

The calculation of each term in this equation will be explained starting with the ablation term. The source term ω_i is positive for the ablation products such as CO and H₂ and negative for the oxidizing species. The enthalpies of each species are taken from NIST [28] database as a temperature-dependent polynomial. The enthalpy of the carbon-graphite nozzle material is, also, taken from the database.

Heat transfer equation for the solid carbon graphite is given in Equation 6.14, assuming the heat conduction in the nozzle graphite is one dimensional and there is a moving local coordinate system tied to the receding surface. Meaning that only the radial direction is important for the heat conduction and heat transfer along the nozzle wall is neglected. Also, steady-state condition assumption is made because the surface temperature rises rapidly in less than 1 s and then it stays relatively constant for the remaining of the burn.

$$\rho_n \frac{\partial h_s}{\partial t} = \frac{\partial}{\partial r} \left(k_s \frac{\partial T_s}{\partial r} \right) + \rho_n r \frac{\partial h_s}{\partial r} \quad (6.14)$$

If we assume that the heat capacity and heat conduction of the solid carbon does not change with the temperature and the outer layer of the nozzle is at a temperature, T_a , Equation 6.15 becomes the analytical solution for the temperature variation in the nozzle. The validity of the assumption of constant heat capacity and conduction is studied by conducting a sensitivity analysis and it is seen that the nozzle erosion rate calculation result is not very sensitive to these variables.

$$T(r) = -C \frac{\kappa}{r} e^{\frac{-rr}{\kappa}} + T_a \quad (6.15)$$

where κ is:

$$\kappa = \frac{k}{\rho C_p} \quad (6.16)$$

The unknown C will be the third unknown along with wall species mass fractions and nozzle erosion rate.

In the surface energy equation, the other term is the radiation effect, which is neglected because it is generally very small in typical rocket nozzle applications compared to the convective heating [29]. Finally, the convective heating effect is calculated by using the Bartz [29] equation. This equation is a crude approximation of the nozzle turbulent

boundary layer solution, but it is assumed that it gives a reasonable approximation for our calculations.

The nozzle erosion rate, species mass fractions at the wall and wall temperature are closely coupled by the Equation 6.1 to Equation 6.16. Therefore, these equations must be solved jointly using an iterative algorithm which gives the nozzle erosion rate contribution of each oxidizing species.

6.2 Discussion of Theoretical Modeling Results

As shown in test results section, in our hybrid rocket motor test firings, micro-aluminum added paraffin-based fuel has decreased the nozzle erosion rate at the throat between 22% to 45% Figure 5.11 and increased the nozzle erosion onset time Figure 5.12. The total aluminum added to the fuel was 7% in mass. The theoretical approach described in the previous section is implemented to explain this improvement for the nozzle erosion and the results are discussed. Only the nozzle throat is included in the calculations because this high mass flux area suffers the worst erosion. Two different cases have been studied with %7 aluminum added fuel and non-energetic-additive paraffin-based fuel. The hybrid rocket motor conditions that are simulated are given in Table 6.3.

Table 6.3 : Hybrid rocket motor parameters for thermochemical nozzle erosion calculation.

Hybrid rocket motor parameters	
Fuel	DY12 (paraffin-based)
Oxidizer	GOX
Equivalence ratio	0.4 to 1.4
Nozzle throat diameter, mm	8.25
Chamber pressure, bar	25
Combustion efficiency	%90
Nozzle material	Carbon-graphite
Nozzle material density, kg/m ³	1840
Additive material	3 μ m Aluminum powder
Additive mass ratio	%7

As described in the previous section, Equation 6.1 to Equation 6.16 are solved by implementing an iterative algorithm and the calculated nozzle erosion rate results are given in Figure 6.3.

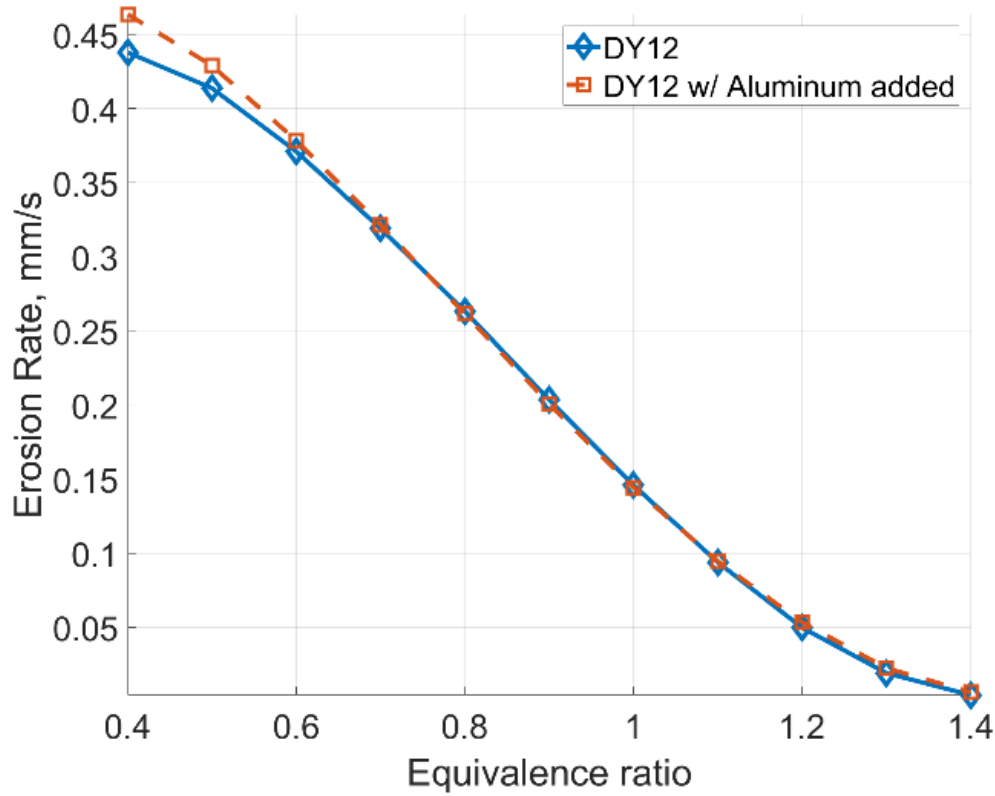


Figure 6.3 : Nozzle erosion rate results with and without aluminum.

The nozzle erosion rate calculation did not give the expected nozzle erosion rate reduction as seen in the experiments. The theoretical calculations given in section 6.1 that even there is a reduction in CO_2 and H_2O oxidizing species mass fractions at the throat by adding aluminum to the paraffin-based fuel which can be seen in Figure 6.4, the substantial nozzle erosion rate reduction by the aluminum addition cannot be explained by this characteristic. The reason for this is that at the operating conditions for gaseous oxygen/paraffin hybrid rocket motor, added aluminum increases the wall temperature by a small amount and decreases the CO_2 and H_2O mass fractions. However, the CO_2 erosion rate contribution by mass fraction is very low compared to other species, so the major effect comes from the H_2O mass fraction reduction and its improvement cannot reach the erosion rate reduction seen in the motor tests. Therefore, it is believed that there must be another mechanism that further reduce the nozzle erosion rate when using a micro-aluminum additive.

Even though there are considerable assumptions when calculating the nozzle erosion rate and nozzle wall temperature, different cases have been studied to understand the sensitivities of the assumptions, but it is seen that the reduction of the nozzle erosion rate by aluminum addition cannot be explained by these theoretical calculations. Therefore, we suspect that the reason for this reduction is because the liquid metal oxide layer protects the nozzle surface from the oxidizing species and reduce the nozzle erosion rate considerably, much higher than the predicted value from the thermochemical nozzle erosion rate calculations.

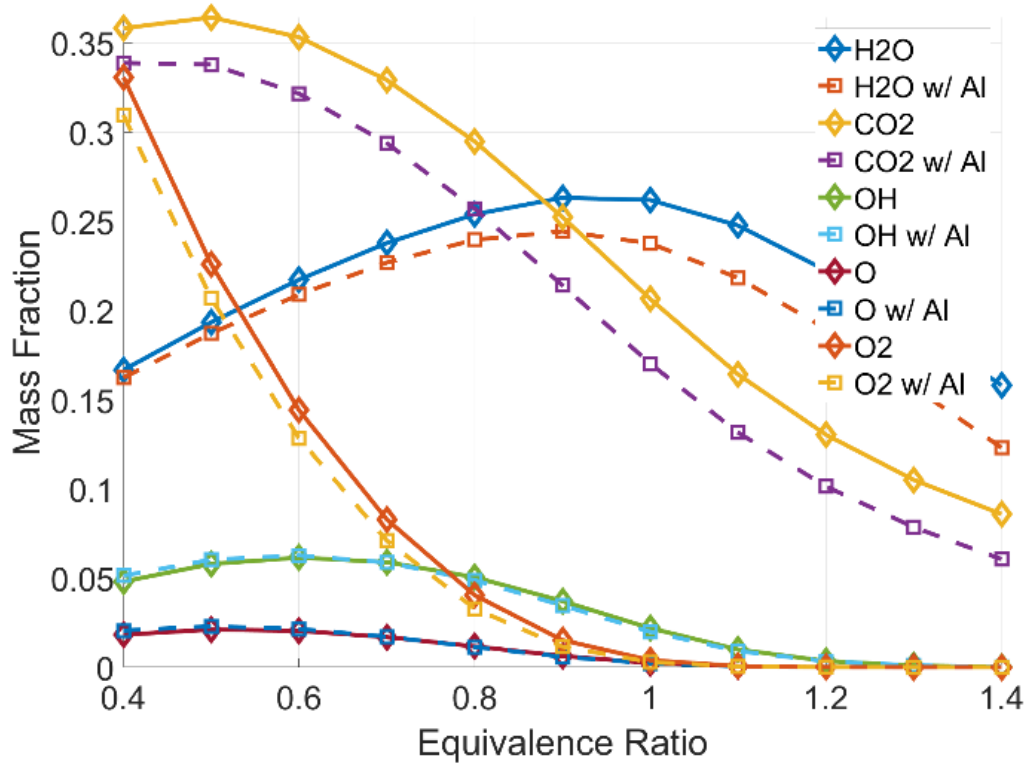


Figure 6.4 : Mass fractions of oxidizing species at the nozzle throat of a hybrid rocket.

One possible explanation for this characteristic is the protection of the carbon surface by the liquid metal oxide layer, Al_2O_3 . Since the Al_2O_3 boiling point temperature is ~ 3250 K, it remains liquid at the nozzle throat. It is plausible that the liquid metal oxide layer could be protecting the nozzle surface from the oxidizing species and reducing the nozzle erosion rate considerably. Photographs of the carbon-graphite nozzles that are used in the tests are shown in Figure 6.5 to Figure 6.8. It can be seen that the nozzle with micro-aluminum added fuel has some aluminum oxide residue on the entrance and expansion sections.

In summary, the characteristics that are seen in the experiments could not be explained correctly by our theoretical approach, and the liquid layer protection by Al_2O_3 explanation is not very well supported. There is a considerable nozzle erosion reduction by aluminum addition, and it is seen that there is an optimum loading ratio, which is 10% by mass Figure 5.13. A more detailed study is needed to explain these phenomena.

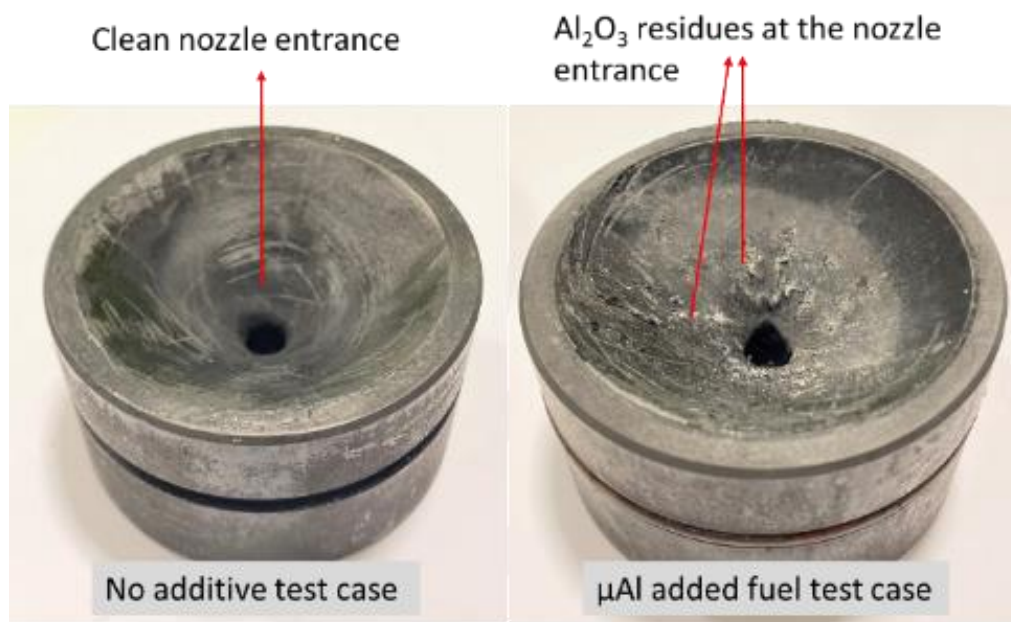


Figure 6.5 : Carbon-graphite nozzle entrance photos for different tests. Al_2O_3 residues are seen in the Al added fuel test case.

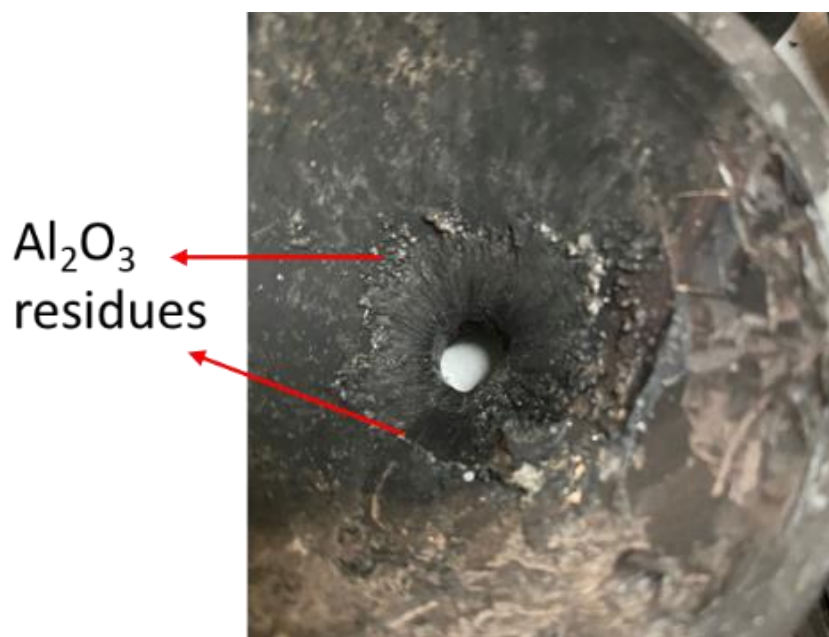


Figure 6.6 : Carbon-graphite nozzle entrance photo for aluminum added fuel after the static motor firing test.

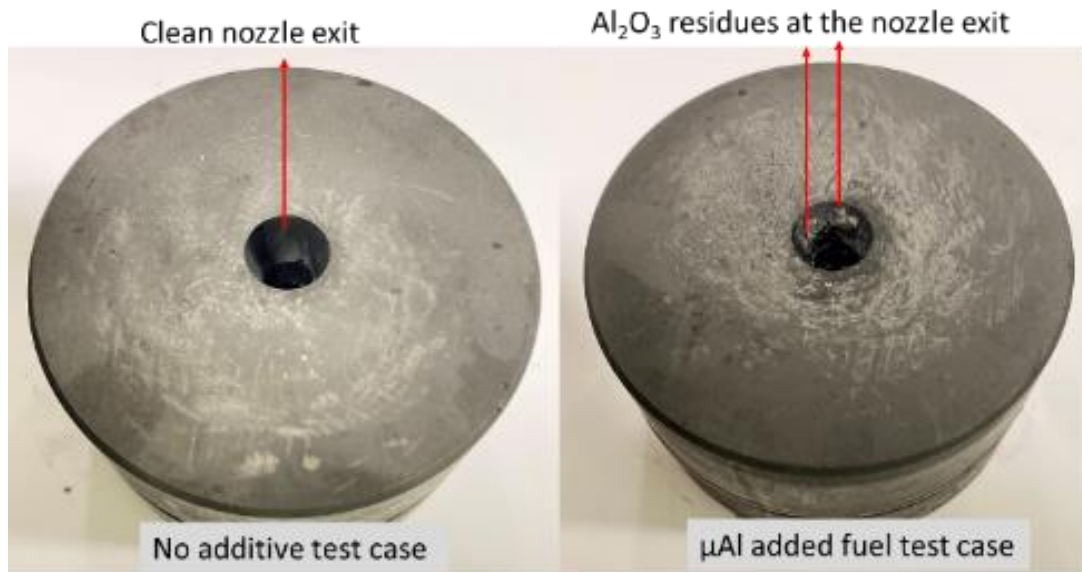


Figure 6.7 : Carbon-graphite nozzle exit photos for different tests.

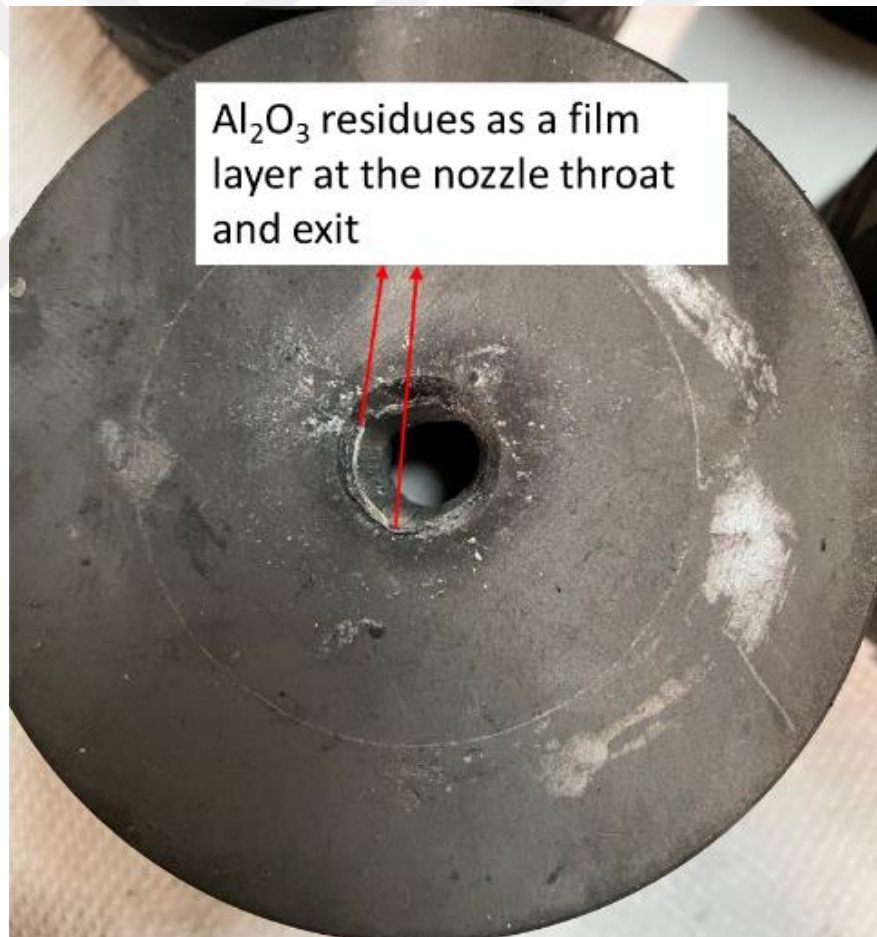


Figure 6.8 : Carbon-graphite nozzle exit photo for aluminum added fuel after the static motor firing test.



7. CONCLUSIONS

We have seen that using performance enhancing additives in order to increase the regression rate of paraffin-based hybrid rocket fuel has no significant improvements. The regression rate results do not justify using these additives which are costly and make the production of fuel harder. From the studied energetic materials, aluminum is a good additive for N_2O_L systems. It increases the I_{sp} performance and reduces the optimum O/F ratio which in turn reduces the required volume for propellant. Also, it helps to reduce the nozzle erosion rate which is a crucial improvement in upper stage rocket motors. Lithium aluminum hydride shows similar performance characteristics to aluminum, but its ratio in paraffin wax is 25% rather than 40% like in Al cases. This suggests that by increasing the $LiAlH_4$ mass ratio, performance can be increased beyond Al fuel cases. However, one disadvantage of $LiAlH_4$ is the cost. Therefore, more small-scale tests should be done to better evaluate this additive performance. Magnesium addition does not show significant improvement, so in future studies it will not be in our focus. Ammonium borane could be a promising material for hybrid rocket fuel additive, but the number of tests in this study were not enough to show its characteristics because of the problems of obtaining this material and the very high cost of the material.

This study shows that there is a considerable nozzle erosion reduction by the addition of micro-aluminum powder to the paraffin-based fuel. Even though the added mass concentration of the aluminum is only 7% by mass, up to 45% reduction in the nozzle throat erosion rate is observed. The novel micron sized aluminum powder addition method to the paraffin-based fuel is scalable and it is very easy to implement. This material addition method to the fuel can be used for other energetic additives such as Mg, $LiAlH_4$ and NBH_6 . This method does not have major effect to the performance of the hybrid rocket motor as shown in regression and erosion rate graphs.

Aluminum addition ratio has a great effect to the erosion rate reduction. 10% by mass aluminum addition maximizes the erosion rate reduction for the hybrid rocket motor that is described in this study. This outcome is an important result and the theoretical calculations steer us to the conclusion that the mechanism of this reduction mostly

comes from the liquid metal oxide layer protection. As an extra note, the disadvantage of AL addition is the reduction in the I_{sp} performance caused by the two-phase flow losses in the nozzle. In our studies we have seen smaller than 1% loss in the I_{sp} compared tests with no additives. Since the optimum aluminum addition ratio is around 10%, the two-phase flow losses are negligible.



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APPENDICES

APPENDIX A: Relative Error Analysis



APPENDIX A: Relative Error Analysis

Data reduction process has its uncertainties and these are estimated by a relative error analysis. In this relative error analysis, the methodology given in Ref. 30 is applied because the same test bench and data acquisition systems are used [30]. The fuel regression rate is one of the critical parameters for motor performance. It is calculated by the initial and final fuel masses as shown in Equation A.1 and A.2.

$$D_f = \sqrt{D_o^2 - \frac{4m_{fuel,final}}{\rho_f L_f \pi}} \quad (A.1)$$

$$\dot{r}_{ave} = \frac{D_f - D_i}{2t_{burn}} \quad (A.2)$$

The fuel and oxidizer mass flow rates are calculated using Equation A.3 and A.4. These are important parameters for performance calculations. The oxidizer to fuel ratio (O/F) is a critical parameter for erosion rate comparisons and it is calculated using Equation A.5.

$$\dot{m}_{fuel} = \frac{m_{fuel,initial} - m_{fuel,final}}{t_{burn}} \quad (A.3)$$

$$\dot{m}_{ox} = A_{inj} C_d P_{tank} \sqrt{\frac{\gamma}{RT_{tank}} \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma+1}{\gamma-1}}} \quad (A.4)$$

$$O/F = \frac{\dot{m}_{ox}}{\dot{m}_{fuel}} \quad (A.5)$$

Relative error in oxidizer mass flow rate E_{mox} could be written in terms of the relative errors in the average feed pressure E_{pf} , orifice diameter E_{do} , orifice discharge coefficient E_{Cd} and tank temperature E_{To} . These four errors in Equation A.6 were determined to be 0.02, 0.001, 0.02, and 0.01 respectively.

$$E_{mox} = \left[E_{pf}^2 + (2E_{do})^2 + E_{Cd}^2 + \left(\frac{E_{To}}{2} \right)^2 \right]^{0.5} \quad (A.6)$$

The relative error in O/F ratio $E_{O/F}$ could be written in terms of the relative errors in oxidizer and fuel mass flow rates, where relative fuel mass flow rate error is selected as 0.01:

$$E_{O/F} = \sqrt{E_{mox}^2 + E_{mf}^2} \quad (A.7)$$

The nozzle throat erosion rate is highly affected by the chamber pressure and its relative error E_{P_c} depends on the sensor sensitivity and maximum sensor operating pressure as shown in Equation A.8. Sensors used in hot fire tests have 0.5% sensitivity at full scale of 70 bar.

$$E_{P_c} = \frac{0.5\% \cdot 70 \text{ bar}}{P_c} \quad (A.8)$$

Finally, the relative error in final port diameter E_{D_f} could be written in terms of fuel grain properties, which are the grain initial and final port diameters. In Equation A.9 relative errors in $E_{\Delta m}$, E_ρ and E_L are determined to be 0.01, 0.011 and 0.002.

$$E_{D_f} = 0.5 \left(1 + \frac{D_i}{D_f} \right) [E_{\Delta m}^2 + E_\rho^2 + E_L^2]^{0.5} \quad (A.9)$$



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