Chapter

Hybrid Propulsion System: Novel Propellant Design for Mars Ascent Vehicles

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Abstract

This chapter briefly introduces hybrid rocket propulsion for general audience. Advantageous of hybrid rockets over solids and liquids are presented. This chapter also explains how to design a test setup for hybrid motor firings. Hybrid propulsion provides sustainable, safe and low cost systems for space missions. Therefore, this chapter proposes hybrid propulsion system for Mars Ascent Vehicles. Paraffin wax is the fuel of the rocket. Propulsion system uses CO_2/N_2O mixture as the oxidizer. The goal is to understand the ignition capability of the CO_2 as an in-situ oxidizer on Mars. CO_2 is known as major combustion product in the nature. However, it can only burn with metallic powders. Thus, metallic additives are added in the fuel grain. Results show that CO_2 increase slows down the chemical kinetics thus reduces the adiabatic flame temperature. Maximum flammability limit is achieved at 75% CO_2 by mass in the oxidizer mixture. Flame temperature is 1700 K at 75% CO_2. Ignition quenches below the 1700 K.

Keywords: hybrid rockets, CO_2 combustion, metallic additives, paraffin wax, mars ascent vehicle

1. Introduction

Mars is known to have the most suitable geological features and atmospheric conditions for the future human spaceflight. Based on the data from the orbiters and rovers sent through deep space, Mars has the most active volcanic mountains and the highest impact craters of all the worlds. Strong evidences via rover measurements moots that liquid water may have poured across the surface of Mars billions of years ago [1]. There is also evidence of methane leakage between rocks that could be an indication of microbial life. Furthermore, the location of Mars smooths the way of long-term human spaceflight. Mars is relatively close to Earth compared to other possible planets that may be explored such as Saturn and Jupiter. Venus is closer candidate however it has very harsh atmospheric conditions. High temperature, high density and corrosive nature of environment makes surface of the Venus challenging to survive.

Although Mars is the best candidate for human exploration, there are some challenges during two-way mission. Mars atmosphere has a density of 0.014 kg/m^3 and pressure of 610 Pa at the surface level. Low atmospheric density indicates that if Mars have had liquid water on its surface, it would have been evaporated immediately. In other words, the atmospheric pressure of Mars should be increased in

order to capture water molecules in atmosphere (at least 6.25 kPa means Armstrong limit). Armstrong limit is also critical for human body resistance. At this limit, breathable oxygen cannot be delivered to body more than a few minutes. Body fluids such as saliva, urine, tears, and alveoli in the lungs would boil away without a special pressurized body suit. Astronauts on Mars can live at this pressure level with a full-body pressure suit.

Human spaceflight to Red Planet takes at least 18 months with at least six months stay on the surface. Therefore, Martian air vehicles are needed both for surface operations and to return to the Earth. Thin atmosphere (due to low Reynolds number) indicates that only air vehicles such as micro helicopters or gliders can operate on Mars's atmosphere. However, these vehicles can only be used for observation purposes and are not feasible for transportation of large payloads. An advanced propulsion system is needed to fulfill mission requirements for long term two-way missions.

Current propulsion systems are quite expensive and technologically not feasible to fulfill two-way mission. In-situ Resources Utilization (ISRU) technologies are required for low cost and feasible propulsion systems. Both air breathing and rocket engines can be used as an ISRU based system. However, airbreathing engines need extremely large inlet areas due to the low atmospheric pressure of the Red Planet. Moreover, the condensed phase combustion products make the turbojet engine impractical. All these circumstances make rocket propulsion systems more practical for Martian operations [2].

Therefore, this chapter proposes a novel propulsion system for Mars Ascent Vehicles. Classical hybrid rocket motor configuration is tested as the propulsion system. The concept is supported by practical motor tests. Hybrid motor uses paraffin wax as the fuel binder and metallic powder as the additive. Aluminum and magnesium are mixed with paraffin as fuel additive. Experiments uses CO_2/N_2O mixture as the oxidizer agent. Combustion process as follows; Nitrous oxide reacts with paraffin and melts the metal oxide layer. Then carbon dioxide burn with metallic additive.

There are several factors to use $Paraffin/Metal/CO_2/N_2O$ propellant combination. 96% of Mars atmosphere involves the CO_2 which is quite promising for in-situ missions. Carbon dioxide is known as a natural combustion product. It has also fire extinguisher feature. However, CO_2 can only burn with metallic powders. Therefore, $Metal/CO_2$ combustion releases significant amount of energy which is quite practical for sustainable Martian operations. CO_2 is self-pressurizing agent that removes the need for an additional pressurizing system in the rocket.

Experimental results show that magnesium has better ignition capability than alumiinum. CO_2 combustion is achieved up to 75% by mass in the oxidizer mixture. Adiabatic flame temperature of the motor is the key parameter for sustainable combustion of the carbon dioxide. Motor ignition quenches below the 1700 K. This is considered as the maximum flammability limit of the CO_2 with paraffin based hybrid motor.

Furthermore, this chapter provides brief knowledge related to hybrid propulsion systems. Hybrids offer safe, reliable, non-hazardous and cost-effective system compared to both liquid and solid systems [3, 4]. Fundamentals of hybrids briefly explained. Common propellant types are stated for hybrid motors. Details of CO_2 based experiments are presented accompanied with fuel grain manufacturing, oxidizer mixing process and combustion characteristics.

2. Hybrid rocket propulsion fundamentals

This section provides fundamental information related to hybrid rocket propulsion. Hybrid rockets provide safety, reliability and environment friendly

manufacturing compared to other conventional rockets. It stores propellants in separate phases as in **Figure 1** [5]. Usually, the oxidizer is in liquid (or gaseous) phase and fuel is in solid phase.

The oxidizer is driven through a main valve into the solid fuel. An injector is used in order to control the oxidizer flow rate. Brass is the common material for the injector due to material properties. Brass is quite durable and resistant to high temperatures. The pressure of the oxidizer is regulated by pressurization system. Helium gas is mostly used as an pressurizing agent. There is an igniter which is placed near the injector manifold for initiating the ignition inside the motor. Igniter compounds moslty consist of potassium nitrate based solid fuels. However, larger rocket motors requires additional igniter motors as presented in [2]. Hybrid rocket motors mostly use circular port grain design. Circular port grains provide easy manufacturing and high regression rates [6]. Combustion occurs inside the grain port by the oxidizer flow and eventually exits through the nozzle. Nozzle throat diameter is designed in order to provide particular chamber pressure inside the motor. Graphite is mostly used for the nozzle manufacturing.

2.1 Hybrid propulsion advantageous

In the solid rocket motors, oxidizer and fuel are mixed as single solid phase. Combustion occurs by heating the solid fuel grain to reach the ignition temperature. Ignition of solid fuel cannot be stopped when it's started thus causes explosive danger. Thrust cannot be adjusted in solid motors that additional control systems are required for the rocket. Liquid motors keep oxidizer and fuel in separate tanks that combustion occurs by mixing propellant in a combustion chamber. Intimate mixture of propellant in a single chamber may cause explosion hazard. Propellant storage also requires exceptional cooling system in pumps, feed system and nozzle.

Hybrid rocket motors, however keeps oxidizer in liquid phase and fuel in solid phase [4]. Oxidizer delivery system (by using single oxidizer tank) reduce the complexity of plumbing compared to liquids. Thus, the ignition can be throttled by a main valve unlike solid motors. Hybrids have inert solid fuel grain thus; the grain manufacturing is safer than solid motors. Besides, it is easy to cast metallic additives in fuel grains to improve the combustion performance. Thus, operation feasibility at low temperatures, long oxidizer storage capability with non-hazardous manufacturing make the hybrids more practical for Mars missions.

2.2 Propellant evaluation in hybrid rockets

Classical hybrid rockets commonly use polymeric fuels such as HTPB (Hydroxyl-Terminated Polybutadiene), HTPE (Hydroxyl-terminated polyether) and PE (Polyethylene). In hybrid motors, a turbulent boundary layer is formed by

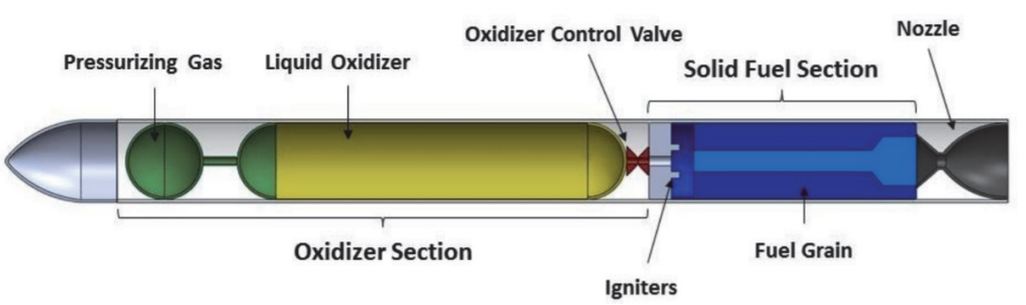

Figure 1.
Paraffin wax liquid entertainment mechanism.

oxidizer injection over the polymeric fuel surface [6]. Thus, the diffusion flame occurs during the ignition at the boundary layer. Diffusion flame is transported on the surface by oxidizer flow. Radiation and convection heat transfer play an important role during this process. Thereby, vaporized fuel on the grain surface reacts with atomized liquid oxidizer causes "blocking effect" at the wall. This blocking effect limits the burn rate of the motor [7].

Paraffin wax is another fuel commonly used in hybrid motors [4]. Paraffin enables 3 to 5 times higher regression rate at the same oxidizer mass flux compared to classical polymeric fuels [6]. Burning paraffin fuel produces a liquid layer over the fuel grain with low viscosity and low surface tension. The liquid melt layer consists of liquified paraffin fuel droplets. This layer merges with the oxidizer flow becomes hydrodynamically unstable in the fuel port. Unstable ignition creates an instability; it lift-offs paraffin fuel droplets from the grain surface that foster the mass transfer rate of fuels into the oxidizer gas flow. This is called as "liquid entrainment mass transfer mechanism" can be seen in **Figure 2** [7]. This additional mass transfer mechanism increases the regression rate of hybrid motor combustion.

Hybrid rockets commonly use N_2O_4 (dinitrogen tetraoxide), H_2O_2 (hydrogen peroxide), gaseous (GOX) or liquid oxygen (LOX) and N_2O (nitrous oxide) as the oxidizer [8]. Nitrogen tetraoxide is storable high-density oxidizer that is used in early launch vehicles. N_2O_4 provides moderate I_{sp} with performance additives. However, it's a high toxic chemical. Hydrogen peroxide is also storable and high-density agent. H_2O_2 is an aggressive chemical at high concentrations. It has leaning to self-decompose thus causes detonation hazard. Typical rocket applications use over 80% concentration levels of H_2O_2 that makes the distillation and handling quite critical for human skin. Liquid oxygen is the most common high-performance oxidizer in the rocket industry. LOX is highly stable due to diatomic oxygen bond and provides high specific impulse. It provides lower oxidizer to fuel ratio that reduces the fraction of oxidizer used in the propulsion system. It is also cost-effective compound. However, LOX is cryogenic material with boiling temperature of 90 K. Cryogenic nature of makes it challenging during surface operations on the Mars. Moreover, liquid oxygen is not self-pressurizing agent due to its low density needs an additional pressurization system via Helium or Nitrogen. This increases complexity and cost of a possible Martian rocket.

Nitrous oxide is another agent has been used mostly in small rocket systems. Nitrous has self-pressurizing capability at saturated liquid state [2]. Self-pressurization eliminates the need of pressurizing system to feed the oxidizer. Thus, it reduces the complexity, weight and cost of the propulsion system.

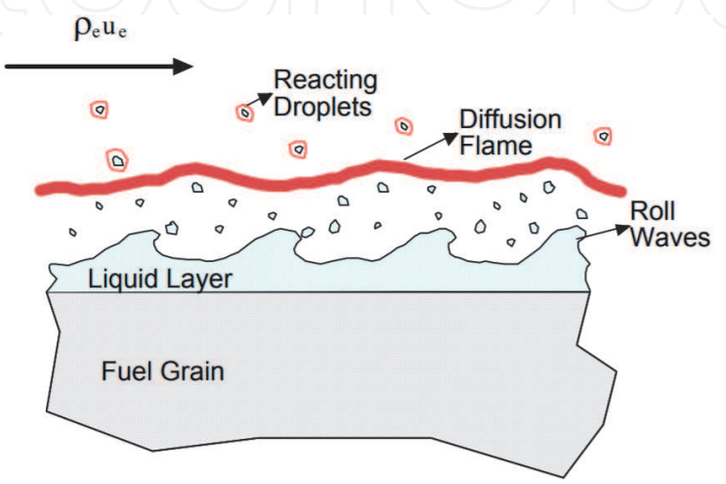

Figure 2.
Paraffin wax liquid entertainment mechanism.

Self-pressurization feature also makes nitrous an efficient candidate for Mars environment. N_2O is non-toxic and easy to handle compared to both N_2O_4, H_2O_2 and LOX. Nitrous oxide also creates a highly exothermic decomposition reaction during the combustion. Therefore, it provides stable and efficient ignition in the rocket systems. Nitrous oxide in liquid phase is quite safe and easy to store at room temperature. Highly storable feature makes launch operations quite easy compared to other oxidizer options. Also, its readily available in chemical industry. On the other hand, reduced specific impulse, low density at higher temperatures and strong dependence of the temperature are among several disadvantages of N_2O. It should be noted that nitrous has positive heat of formation. Thus, self-decomposition of "vapor phase" nitrous in feed lines, oxidizer tank and combustion chamber result disruptive damage [9].

2.3 CO_2 as a novel oxidizer

Carbon dioxide is known as a natural combustion product from hydrocarbons or explosions. However, there are certain fuels that remove the carbon–oxygen bond in the CO_2. That is to say metals have higher reactivity series compared to carbon thus removes the carbon oxygen bond. This reaction produces a substantial energy release. Various metals and metal hydrides have been studied in order to understand the combustion characteristics of carbon dioxide as explained in [2, 10–12]. In addition, additional information is presented related to the $Metal/CO_2$ combustion in Chapter 3. However, fundamental findings from [2, 10–12] are explained in this section.

Kara and Karabeyoglu [2] provides practical experiments by using CO_2 as the oxidizer in lab scale hybrid motors. CO_2 is mixed with the nitrous oxide to understand the combustion characteristics. Paraffin based fuel consist of 40 % aluminum powder by mass. Aluminum powder has 3 micron spherical shape. Al has two purity levels 98.75 % and 99.99 %. The purity level has no significant effect on carbon dioxide combustion. According to [2], succesfull combustion is achieved up to 45 % by mass in the oxidizer mixture. In his comprehensive study, Boiron [10] explains the in-situ resources utilization techniques for hybrid propulsion based Mars Ascent Vehicles. Boiron promotes high performance liquid oxygen/paraffin based hybrid rocket system. He proposes two concept missions; Mars Sample Return (36 kg payload mass) and Medium-scale (500 kg payload) Rocket. Borion explains background on in-situ propellant production techniques by using electrolysis methods. He discusses advantageous and disadvantageous of Paraffin/Aluminum/ O_2 / CO_2 propellant combination for Martian rockets. Finally, Boiron presents details Zirconia cell hardware and electrochemical mechanism. Other fundamental researches related to carbondioxide combustion are studied by Shafirovich Gokalp and Zubrin [11, 12]. Shafirovich and Gokalp presents the concept of a metal/carbon dioxide propellant for Mars Sample Return missions. They provide detail thermochemical analysis of CO_2 combustion with various of metals and metal hydrides in rockets. In addition, they provides lab scale combustion experiments with the magnesium. Shafirovich and Gokalp compares several designs for their ascent/decent vehicle such as hybrid engine, liquid monopropellant engine and bipropellant engine. Robert Zubrin who is one of the pioneer scientist in the field of Mars missions proposes diborane and silane for Mars Ascent Vehicles.

Although there are many theoretical studies on $Metal/CO_2$ combustion, it has not been tested in actual hybrid rocket motor. There is an experimental study on combustion characteristics of carbon dioxide with magnesium rocket engines [13]. Yue Lie uses magnesium fuel in powder form with multiple gas injection mechanisms into the combustion chamber at high pressures. Yue presented the

thermodynamic calculations for the combustion process of the multiphase flow environment in a lab scale rocket engine used in the experiments. However, this design seems impractical that gas phase oxidizer needs pressurizing system.

2.4 Metallic powder additives

Metallic powders serve as excellent fuel additives due to their significant volumetric and gravimetric heat release during the combustion process [8]. Purity, size and shape of metallic powders directly affect the combustion performance as they control the ignition delay and the formation of the condensed combustion product (CCP).

Wide range of additives have been studied for CO_2 combustion in rocket motors such as lithium (Li), boron (B), berillyum (Be), aluminum (Al), magnesium (Mg), magnesium hydride (MgH_2), diborane (B_2H_6) and silane (SiH_4). Lithium is highly reactive alkali metal however shows volumetric heat release is low (means low specific impulse) additives due to its low density. Boron is commonly used as a solid propellant additive. Despite it has high combustion energy per unit mass, it delivers poor combustion efficiencies. Major concern of boron is reveals high CCP in the nozzle. Magnesium hydride increase specific impulse however not practical for longer lifetime missions due to its poor dehydrogenation kinetic and hydrogen storage. Casting and lifetime are major issue for all other metal hydrides.

Figure 3 shows the theoratical specific impulse values with respect to oxidizer to fuel ratio. Calculations are made by [11] with 10 bars of chamber pressure.

Diborane is storable at 5 bars in Martian conditions. Diborane shows high mass fraction of CCP effects the specific impulse. Boron oxide formation in liquid form generates a significant risk for slag formation in nozzle throat. Decomposition is

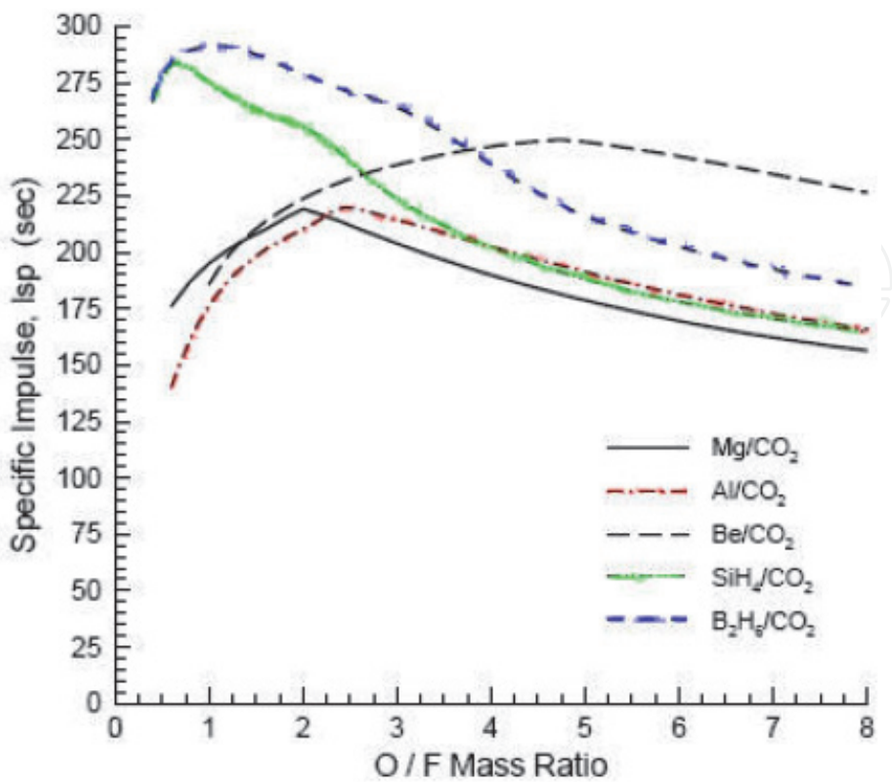

Figure 3.
O/F ratio versus specific impulse – Various of additives.

another factor for diborane. Silane has silicon oxide as the major CCP. It provides lower mass fraction of CCP than diborane. However, silane is quite toxic there is not enough reliable data for SiH_4/CO_2 combustion [10, 12].

Therefore, analysis shows that beryllium, aluminum and magnesium are most prominent candidates for carbon dioxide combustion due to performance and safety aspects. Beryllium is extremely toxic despite its high performance. All in all, magnesium and aluminum are left over as major additives casted in the paraffin wax.

2.5 Aluminum and magnesium combustion with the CO_2

Aluminum is low cost and widely used as micron/nano sized metallic powder form. Both spherical and flake shaped aluminum can be casted easily within paraffin wax. Aluminum provides high specific impulse with the CO_2. However, Al/CO_2 combustion produces severe slag formation results nozzle blockage due to oxide (Al_2O_3) formation. Magnesium is can also be found broadly in the market. Mg shows rapid ignition characteristics in carbon dioxide environment due to its low ignition temperature of 1000 K. In addition, metal oxide layer of a magnesium powder sphere is not strong as in aluminum that is easily breakable during combustion. Therefore, magnesium oxide (MgO) formation by Mg/CO_2 reaction is not as severe as in aluminum oxide. It shows less particle agglomeration and two-phase losses in the nozzle.

3. Propellant design for Mars ascent vehicles

This section refers the proper propellant combination for the Mars missions. Mars hoppers, ascent vehicles or any rocket systems can use the proposed propellant combination. Both aluminum and magnesium are proposed as main additive. Paraffin wax is the main binder. In addition, hybrid rocket system uses in-situ CO_2 as the major oxidizer. However, since the pure carbondioxide combustion poses several challenges due to reduces chemical kinetics, N_2O/CO_2 oxidizer mixture is selected for performance analysis.

3.1 Fuel grain manufacturing

Paraffin wax $(C_{32}H_{66})$ is the main binder of the solid fuel grain. Hydrophobic nature of the paraffin protects the metal additives from the water vapor. It is nontoxic thus produces water and carbon dioxide as combustion product. Paraffin has low glass transition temperature $(-180°C)$ that is quite feasible colder periods of Mars atmosphere. Also, inert feature of the paraffin wax is feasible for long duration Mars missions [2, 8].

3 micron sherical shaped aluminum is casted up to 40% by mass in the paraffin. In addition, flake shaped aluminum powder is also tested. Combination of 20% flake 40% spherical aluminum-based fuels have higher carbon dioxide concentration during the combustion. Surface area of flakes are larger than spheres thus initiate the combustion easier. Magnesium is also used in actual motor experiments. 44-micron magnesium powder has 99.99% purity level. Mg amount in paraffin is 60% by mass.

Mixing metallic powders up to 40% by mass is achieved by using Silverson L5M high shear mixer [14]. High shear mixer uses square shaped blades. Mixing metal additive with paraffin binder as follows,

- The required quantity of pure paraffin wax is heated and liquified through a beaker. Then, desired" Structural Additives" are added in the paraffin wax

- Paraffin based formulation mixed again with the High Shear Mixer for 2 minutes at 5000 rpm in order to provide a homogeneous mixture.

- The required quantity of metallic powder is added to the molten paraffin fuel

- Silverson L5M High Shear Mixer at 6000 rpm is used to mix powders uniformly in the molten paraffin wax at 120 °C for 5 minutes to ensure homogeneity

- Liquid binder/additive mixture is casted axially into a phenolic mold that is kept around 80 °C. Thus the fuel grain is allowed for cooling to room temperature. The cooling process takes around 5 hours.

- Finally, fuel grain is machined to the intended circular port and outer diameter.

The **Figure 4** shows the several fuel samples that are casted with the L5M High Shear Mixer. It is worth to note that, although high shear mixer allows homogenous mixture of paraffin and metal powders, increasing magnesium amount to 60% cannot be casted by using high shear mixer due to high viscosity. The structure of 60% magnesium 40% paraffin mixture is like mud that only be casted by hand-mixing in a phenolic mold.

3.2 The oxidizer selection

Hybrid Mars Motor experiments uses CO_2/N_2O oxidizer mixture in blowdown mode. Self-pressurizing capability of both oxidizers makes Martian operations quite practical. In addition, the mixture displays several advantageous such as (i) improved I_{sp} performance compared to pure CO_2, (ii) decreased two-phase losses due to reduced mass fraction of condensed phase products (CO_2 allows additional burning with the condensed phase species), (iii) low freezing point of the oxidizer mixture is ideal for Martian environment (iv) both agendst has self-pressurizing feature that not require any additional pressurizing system in the rocket, (v) low cost, less complicated and lighter compared to liquid bipropellant engines.

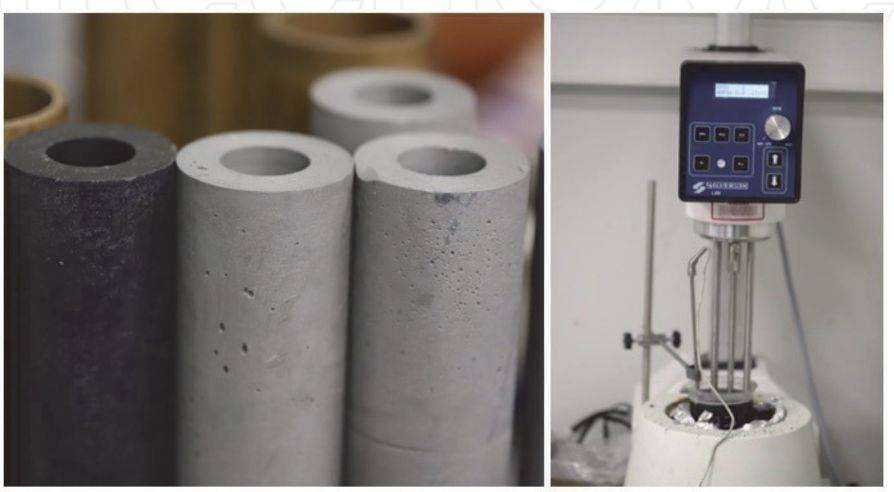

Figure 4.
Fuel samples and Silverson L5M high shear mixer [?].

Uniform mixture of N_2O and CO_2 is achieved due to similar fluidic characteristics of agents. **Table 1** summarizes physical characteristics due to NIST database [15].

Mixing two self-pressurizing saturated liquids requires careful process. Actual motor experiments uses 10 liters aluminum scuba tank with maximum operating pressure of 200 bars is the main oxidizer tank. The oxidizer compound that has higher mass fraction first filled in the scuba tank. Then the tank is vented to cool the oxidizer and reduce the tank pressure around 30 bars. The reduced tank pressure allows second oxidizer (source tank that has higher pressure) compound to add the scuba tank. Therefore, the second oxidizer compound is then added in main tank.

Oxidizer mixture density is the major parameter for the performance analysis of the ignition. Specific volume of the mixed oxidizer is found by using the specific volumes of the components and the mass fraction (χ) of N_2O in the mixture.

$$\overline{v}_{liquid} = v_{N_2O}\chi + v_{CO_2}(1-\chi) \tag{1}$$

The overall oxidizer density is calculated, by assuming an ideal mixture, using simple formula,

$$\overline{\rho}_{liquid} = 1/\overline{v}_{liquid} \tag{2}$$

Liquid N_2O and CO_2 mixture operates in blow-down mode during experiments. The oxidizer mixture has two-phase flow characteristics in the feed system through the injector. The oxidizer flow is choked at the injector thus downstream pressure (motor chamber pressure) has no effect in the flow rate. A blow-down oxidizer mixture needs an advanced approach by using two phase physics. Because, self-pressurizing N_2O or CO_2 in saturated liquid state cannot be modeled by using fundamental ideal gas, compressible or incompressible flow assumptions. Two phase flow approaches by using Homogeneous Equilibrium Model (HEM) is needed for more precise calculations on flow rate and discharge coefficient.

3.2.1 Two phase flow background

Typical rocket applications require fluid dynamics calculations of the injector and propellant feed system. Most of the liquid propellants such as hydrogen peroxide (H_2O_2), ethanol (C_2H_5OH), RP-1 $(C_{12}H_{24})$ and nitrogen tetraoxide (N_2O_4) can be modeled accurately by using classical incompressible fluid dynamics features. In addition, gaseous propellants such as gaseous oxygen, hydrogen and methane use ideal gas law and compressible fluid assumptions. Liquid oxygen (LOX) can also be

T_{tank}, °C	P_{tank}, bar N_2O	P_{tank}, bar CO_2	ρ_{N_2O} kg/m^3	ρ_{CO_2} kg/m^3	v_{N_2O} m^3/kg	v_{CO_2} m^3/kg
0	31.21	34.85	909	927	0.0011037	0.0010782
5	35.40	39.69	884.28	897.26	0.0011354	0.0011160
10	39.99	45.01	856.48	863.64	0.0011735	0.0011613
15	45.03	50.87	824.11	823.33	0.0012185	0.0012177
20	50.55	57.29	785.27	772.28	0.0012737	0.0012930
25	56.60	64.35	737.61	705.05	0.0013460	0.0014075
30	63.25	72.10	678.29	614.56	0.0014533	0.0016855

Table 1.
Saturation properties of N_2O and CO_2.

modeled accurately. Although LOX is in a saturated state at cryogenic temperatures, it uses single-phase incompressible flow assumptions. Compressibility (Z) factor of liquid oxygen at 1 atm pressure is 0.004, and 0.97 for saturated cryogenic oxygen vapor. Both values are very close to ideal values 0.0 and 1.0 [16, 17].

Nitrous oxide however has a liquid Z factor of 0.13 and saturated vapor compressibility factor of 0.53 at the room temperature. Therefore, incompressible liquid or ideal gas assumptions become inaccurate for modeling nitrous oxide. N_2O is handled as a two-phase mixture for fluid flow modeling. Two-phase flow modeling means that fluid flows as a mixture of liquid phase and a vapor phase at the same time. A fluid quality factor is required for the fluid flow. Fluid quality is the ratio of the vapor mass fraction divided by the total fluid mass.

Injector modeling of self-pressurizing agents such as nitrous oxide is a complex process [17]. Because, fluid quality factor changes during tank evacuation; liquid phase boils into vapor phase. Therefore, internal tank pressure and fluid density changes during the evacuation. Tank pressure and fluid density directly effects the injector mass flow rate calculations. And changing the mass flow rate directly effects the combustion stability, motor pressure and thrust.

4. Hybrid motor design & propellant performance

This section presents the performance results for $C_{32}H_{66}/Mg/N_2O/CO_2$ and $C_{32}H_{66}/Al/N_2O/CO_2$ propellant combination. Theoretical specific impulse with respect to O/F (oxidizer to fuel) ratio is determined by NASA's Chemical Equilibrium Analysis (CEA) software [18]. Combustion energies of selected propellants are also explained. In addition, hybrid motor design is presented in this section. CAD drawing of the actual motor is presented accompanied with the real ignition process.

Carbon dioxide combustion slows down the chemical kinetics in the motor. This reduces the adiabatic flame temperature of the motor. The combustion boundary of experiments are depending on the adiabatic flame temperature limit. Therefore, the major goal of this section is to present the flame temperature change due to carbon dioxide addition in oxidizer mixture.

4.1 Thermochemical analysis of propellant combination

The **Figure 5** shows the $O/F \ \ vs \ \ I_{sp}$ for magnesium based propellants. Magnesium is loaded as 60% by mass. CO_2 mass fraction is 70% by mass in the oxidizer mixture. Chamber pressure, combustion efficiency, and area ratio are taken as $38 \ bars, \ 0.98 \ and \ 70$. Ambient pressure is selected as 0.006 bar which is Martian atmospheric pressure value.

Magnesium and carbon dioxide addition to propellant combination clearly reduces the O $/F$ ratio. Carbon dioxide increase in nitrous to 70% shifts to O$/F$ ratio throughout 1. Reduction in O$/F$ has the advantage of lower oxidizer mass tank. This further reduces the required nitrous mass brought from the Earth in a possible Mars Ascent Vehicle design.

The **Figure 6** shows the $O/F \ \ vs \ \ I_{sp}$ for aluminum based propellants. Al mass fraction is 40% in the paraffin. CO_2 mass fraction is 50% in the oxidizer mixture. Chamber pressure, combustion efficiency, and area ratio are taken as $38 \ \ bars, \ 0.90 \ and \ 70$.

In **Figure 6**, although theoretical calculation assumes 90% combustion efficiency, practical Al/CO_2 based experiments show actual combustion efficiency of

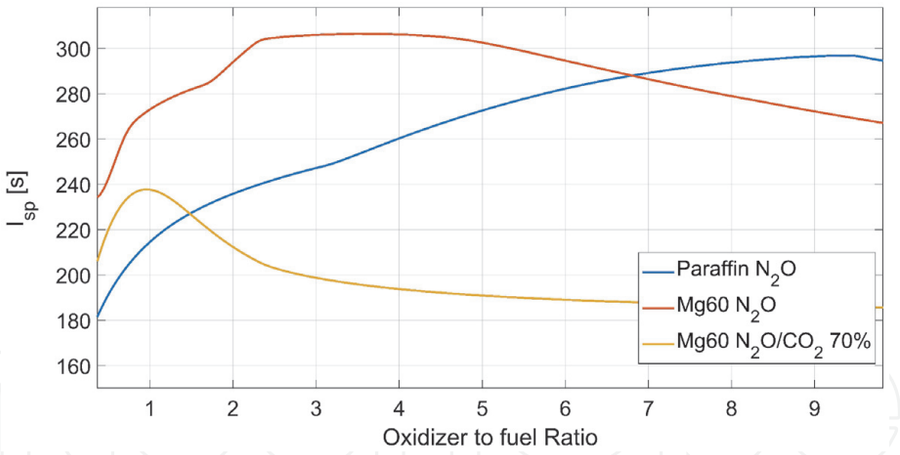

Figure 5.
O/F ratio versus specific impulse – Magnesium based.

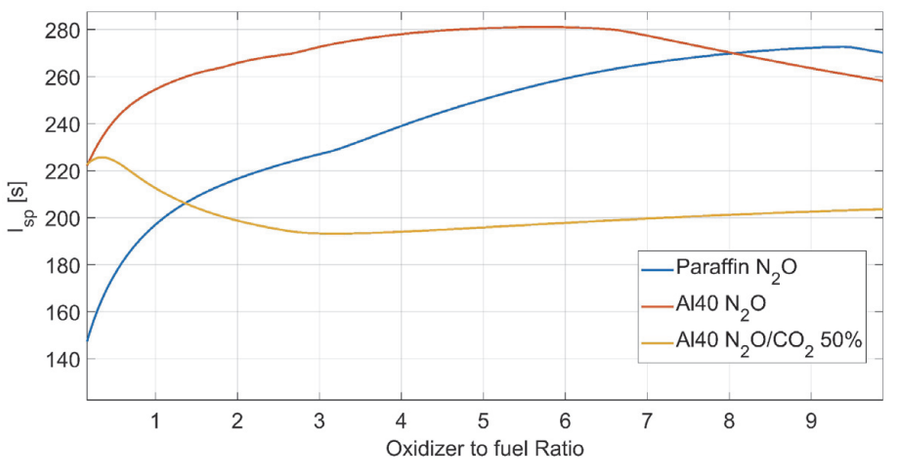

Figure 6.
O/F ratio versus specific impulse – Aluminum based.

70%. Therefore, theoretical I_{sp} of aluminum-based experiments is found as 125 seconds at O/F ratio of 0.5. This shows that magnesium provides better performance and efficiency for MAVs.

4.1.1 Released energies of propellants

Energy analysis is useful indicator of the propellant performance. The energy release due to the combustion is calculated by using heat of reactions (Q_R) of chemical compounds (products and reactants). The Eq. 3 is the formulation for the heat of reaction (combustion) in kJ/kg for the specific propellant. In this equation, $\tilde{Q}_c$ is the heat of formations of products minus reactants. n_m is the mole number and MW is the molecular weight of propellants (reactants).

$$Q_R = \frac{\tilde{Q}_c}{\sum (n_m MW)_{propellant}} \tag{3}$$

$\tilde{Q}_c$ refers the difference between total heat of formations of products and reactants at 25°C.

$$\tilde{Q}_c = \sum_{products} \Delta\tilde{H}_{f@25°C} - \sum_{reactants} \Delta\tilde{H}_{f@25°C} \tag{4}$$

Propellant Type	Mass fractions	Optimum O/F Ratio	$T_{flame,max}$ K	E_{prop} kJ/kg
$C_{32}H_{66}/Mg/N_2O$	Mg40	5	3385	5801
$C_{32}H_{66}/Al/N_2O$	Al40	5	3570	6962
$C_{32}H_{66}/Mg/N_2O/CO_2$	Mg60 $CO_2$70	0.8	2350	5795
$C_{32}H_{66}/Al/N_2O/CO_2$	A160 $CO_2$70	0.7	2550	5639
$C_{32}H_{66}/N_2O$	-	8	3263	5307

Table 2.
Released Energy Values of Propellants.

Energy analysis of various propellants presented in **Table 2**. Energy releases per kg of propellants is presented due to adiabatic flame temperature at the optimum O/F ratio. **Table 2** shows the fuel additive and carbon dioxide mass fractions and released energy ($Q_R = E_{prop}$) per kg of propellant. Results are negative that means reactions are exothermic.

Table 2 indicates that aluminum provides 35 percent higher energy than the magnesium in N_2O ignition. Furthermore, released energy of 70 % CO_2 based propellant is almost same as *Paraffin/Nitrous* propellant. This means that, although carbon dioxide slows down the chemical kinetics, it provides same energy level as *Paraffin/Nitrous*. Al and Mg provides similar heat of reaction for 70% CO_2. Al and Mg with carbon dioxide provides higher heat of reaction than 70% CO_2 based propellants.

4.2 Rocket motor design

A classical hybrid rocket motor is designed for the experiments. **Figure 7** illustrates the motor layout. The hybrid rocket motor consists of stainless-steel pre-combustion chamber with 3 grams solid fuel-based pyro section. The pyro is powered with 24 V battery. Pyro releases 5 kW to heat up the motor in 5 seconds. Brass injector chokes the flow therefore downstream pressure has no effect in flow rate. Brass retainer plate is significant to tether the injector. Oxidizer flow rate changes between 40 and 250 grams per second. Graphite insulator in pre-combustion chamber incarcerates the heat of the pyro fuel. There is a pressure transducer to measure downstream pressure (motor chamber pressure).

Combustion chamber has the 2.5 mm thick phenolic layer for the grain insulation. Single port fuel grain is 180 mm in length. Inner port diameter is 24 mm.

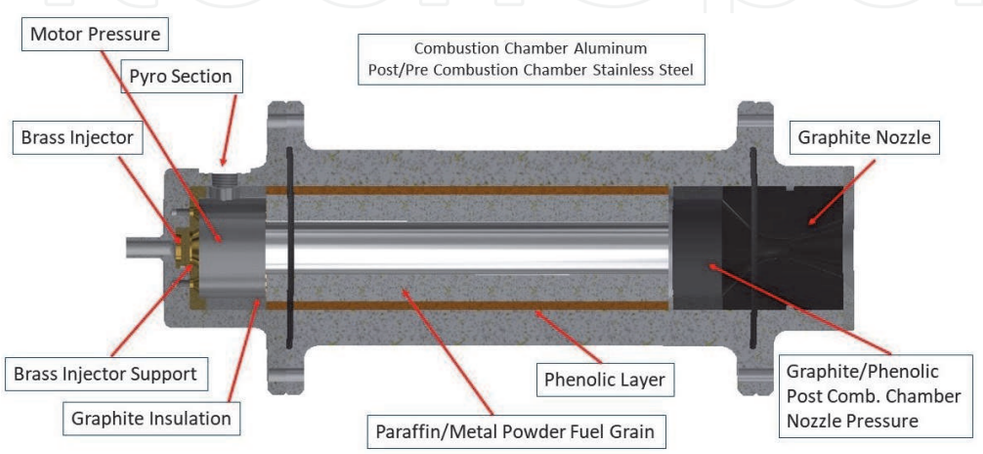

Figure 7.
Mars hybrid rocket motor lay-out.

And the outer grain diameter is 48 mm. Post combustion section has phenolic based layer to absorb the ignition. Nozzle (post combustion) pressure is also measured by the pressure transducer. Motor nozzle is made out from graphite. The throat diameter from 5 to 11 mm to regulate the combustion pressure.

4.2.1 Motor ignition process

The ignition of starts with 2.5 seconds of nitrous combustion (nitrous boost stage). This step exposes enough heat into the motor to take CO_2 combustion easy. Thus, carbon dioxide based combustion (main ignition stage) takes place with an energy boost. The **Figure 8** shows the actual experiment and the test bench.

4.2.2 The complete test setup

The **Figure 9** shows the complete test setup including nitrous boost stage, main ignition stage and purge lines. Nitrous boost stage uses the Aluminum 6061 based oxidizer tank with maximum operating pressure of 280 bars. Nitrous oxide is stored around 50 bars. Nitrous line consist of Mv (manual) and Av (automatic) valves for the operation. Purge line uses the same tank as Nitrous line. Purge tank stores 30

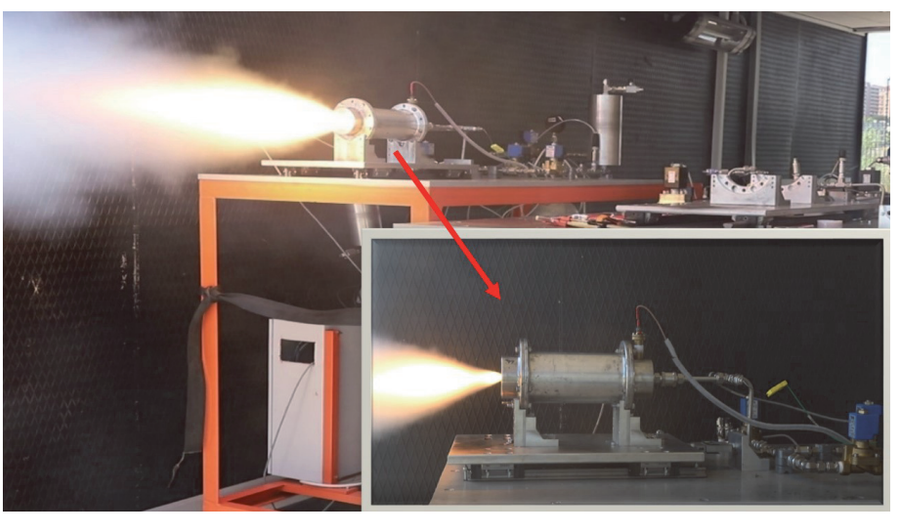

Figure 8.
Actual experiment images.

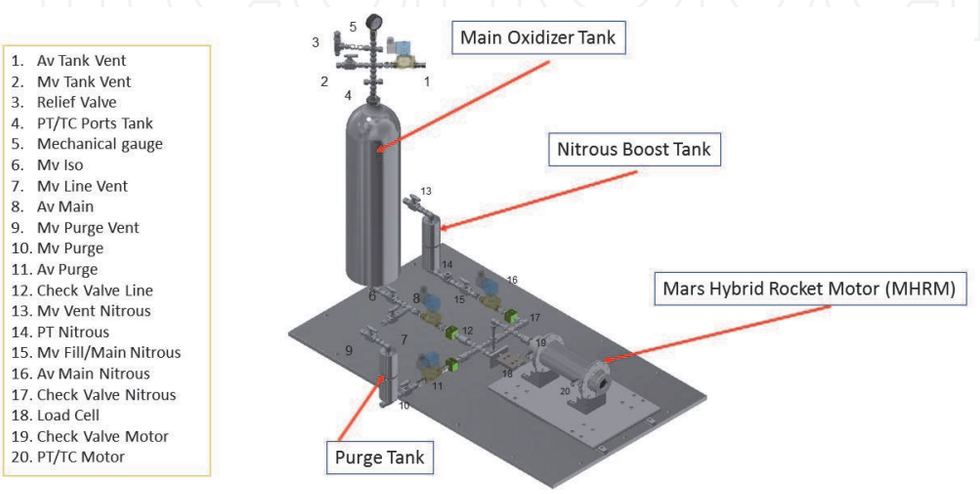

Figure 9.
The complete test setup.

bars nitrogen to cool down the motor after the ignition. Main oxidizer tank is a 10-liter aluminum tank, includes CO_2/N_2O mixture in "blowdown" mode. Main tank has relief with 90 bars cracking pressure. Tank also has vent valves. In addition, mechanical pressure gauge shows the oxidizer pressure as a backup of the National Instruments DAQ system [19].

Check valves are used in all feed lines as well as just before the motor entrance. Check valve prevents hydrocarbon fuel leakage through to nitrous lines. If the nitrous vapor phase interacts with the hydrocarbon, it suddenly decomposes into nitrogen and oxygen (releases +19.5 kcal/mole energy). Karabeyoglu [9] experienced decomposition hazard of nitrous due to deflagration wave as sudden pressure increase from 52 bars to 900 bars in 3 seconds. A K-type thermocouple is used to measure the temperatures. Pressure transducer has measuring efficiency ± 0.5% of the full measurement scale of 70 bars with repeatability that is better than ± 0.05%. Pressure/temperature are recorded by using a National Instruments Data Acquisition System and Lab View signal express software. The sampling rate of the DAQ system was set to 5120 Hz. Detail sensitivity features in error analysis is explained in appendix section of this thesis.

5. Combustion boundary of the CO_2

The motor chamber pressure (adiabatic flame temperature) is the key factor to achieve a successful combustion. Combustion quenches below a certain T_{flame} level. Thus, T_{flame} profile of Al tests is shown in **Figure 10**. Aluminum mass fraction in the paraffin wax is increased up to 60% (60% Aluminum and 40% Paraffin wax). In the fuel grain, 20% of this content is casted as 3 micron flaked shaped Al, and 40% is casted as spherical shaped aluminum. Flake shaped powder has larger surface area that forms better ignition characteristics. Thus, successful combustion limit is increased up to 55% CO_2. However, this limit is considered as "stochastic limit" since there are also ignition failures.

Adiabatic flame temperature has different profile in Mg based experiments. Thus the **Figure 11** shows T_{flame} variation due to CO_2 addition at hybrid motor experiments. Combustion quenches (fails) below a certain T_{flame}. The stable ignition occurs at 75% CO_2 level around 1700–1800 K. Ignition quenches below the 1700 K.

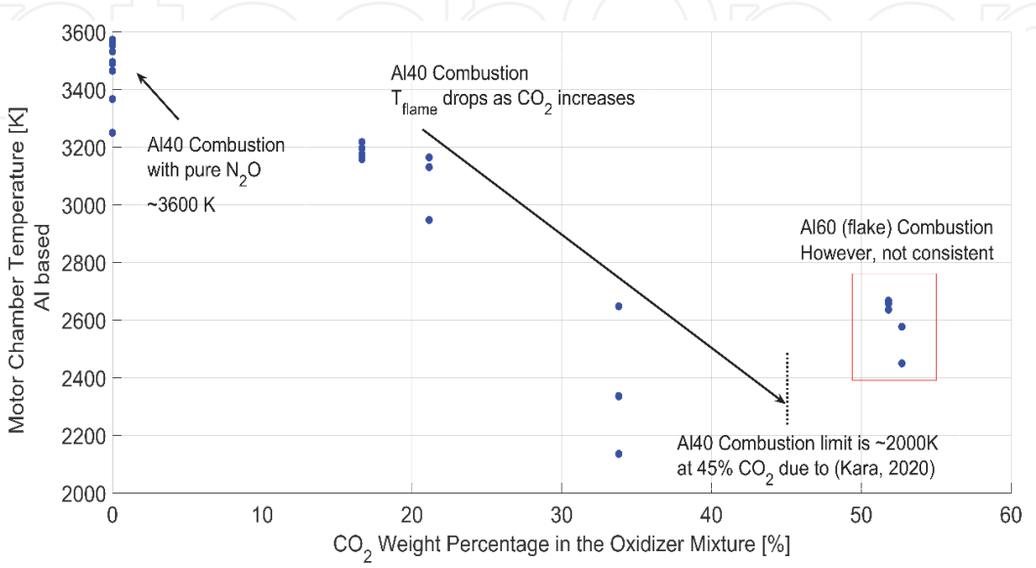

Figure 10.
Flammability limit of Al/CO_2 experiments.

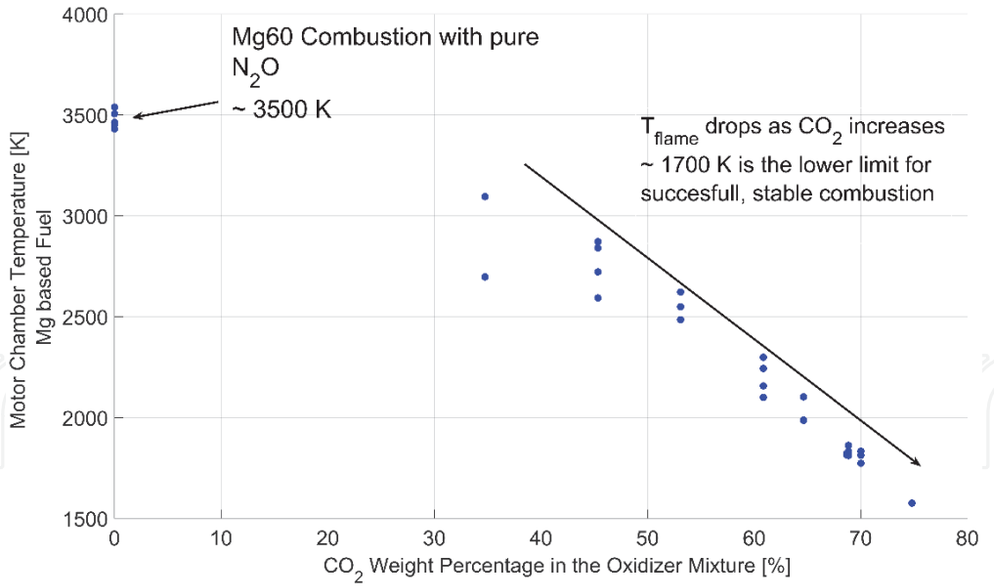

Figure 11.
Flammability limit of Mg/CO_2 experiments.

Figures 10 and **11** show Mg can easily ignites up to 75% carbon dioxide by mass in the oxidizer mixture. Mg has easier ignition capability than the aluminum. For example, flame temperatures of Mg and Al at 35% carbon dioxide are 3000 K and 2400 K. Although aluminum mass fraction increases to 60%, ignition fails around 55% CO_2 level.

Combustion boundary of the CO_2 due to the flame temperature is compared with the literature [20]. In this study, Reina et al. showed the flame temperatures both aluminum and magnesium in CO_2 environment between 1 and 10 bars. Various of powder sizes in micron level are studied. Literature survey by Reina explains that micron sized aluminum has around 1800 K ignition temperature with the carbon dioxide. However, Reina uses nano sized aluminum in their study. Thus, results showed that nanoAl has ignition temperature around 1000 K. Furthermore, ignition temperature is changing between 900-1000 K micro Magnesium based powder.

Therefore, results shows that ignition fail around 1600 K using the $Paraffin/Mg/N_2O/CO_2$ propellant. Also, ignition temperature of Mg/CO_2 is found as 1000 K in the literature. This means that excessive 600 K (or more) can be used to vaporize the paraffin wax during the combustion. If the heat required to vaporize paraffin is excluded, the combustion quenches. The increased internal ballistics is needed to achieve higher amount of CO_2.

Combustion mechanism of Metal/CO_2 based propellants also discussed due to oxidizer mass flux of the rocket. Flux dependent results are significant for scale up rocket motor design. The ignition limit also stated as averaged mass flux versus adiabatic flame temperature. **Figure 12** shows that the combustion quenches at motor chamber pressure (adiabatic flame temperature) below the 1600 K. So, the yellow zone is practically impossible region due to ignition boundary. Red dots states the quenched ignitions. In addition, 1000 K is the theoretical combustion value of Mg/CO_2 due to [11, 12] Therefore, the blue zone is theoretically impossible zone for the combustion. Practically possible zone is shown as orange region. Paraffin/Mg based hybrid motor that operates in this region successfully ignites CO_2. There is a quenched ignition point at average mass flux of 375 kg/m^2s for 70 % CO_2. Details of this analysis are explained in PhD thesis version of this book chapter by Kara.

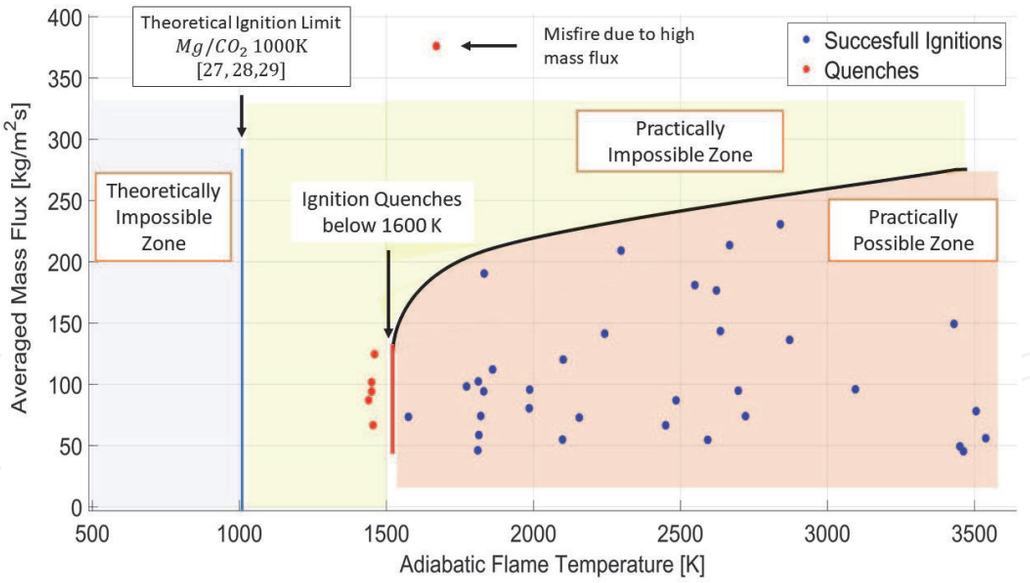

Figure 12.
Oxide formation after the motor experiment.

5.1 Issues during the combustion

Hybrid rocket experiments reveal a significant issue during the combustion. That is the slag formation due to condensed combustion products (CCPs). CCP means the oxide formation as the combustion product. Aluminum (or magnesium) combustion produces aluminum oxide (or magnesium) oxide that has no effect on the combustion performance. Because, combustion performance such as thrust and specific impulse are only formed by the gaseous products. After experiments, 8% of fuel residual is oxides. **Figure 13** shows the motor condition after the experiment. Oxide formation blocks. In addition, poor-quality fuels can be wrapped during the experiment thus blocks the nozzle and the injector.

It is worth to note that although oxide formation reduces the performance, it blocks the nozzle throat and increases the motor chamber pressure during experiment. Therefore, increasing motor chamber pressure causes high efficiency combustion.

5.2 CO_2 combustion: subsequent improvements

subsequent studies will focus on alternative methodologies to achieve higher carbon dioxide combustions. There are several methods that can be considered such

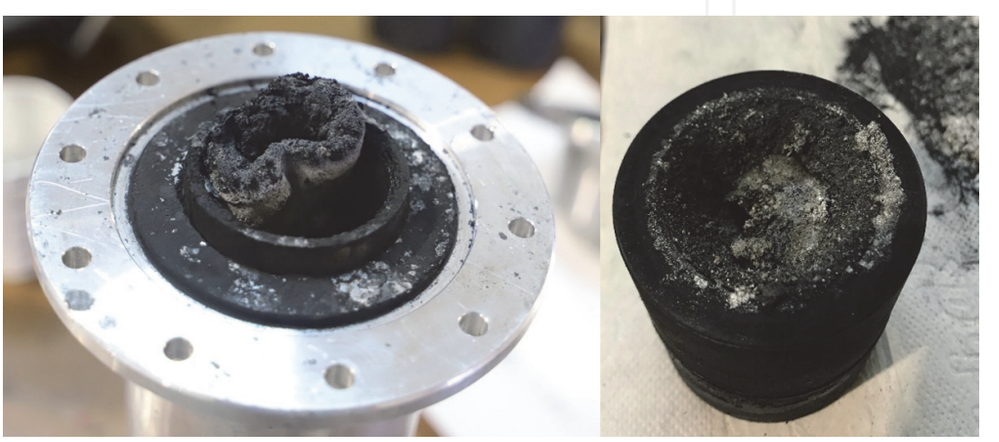

Figure 13.
Oxide formation after the motor experiment.

as (i) magnesium additive mass fraction increase in paraffin wax (up to 80%), (ii) aft injection methodologies to increase adiabatic flame temperature, (iii) Potassium nitrate addition into the fuel grain, and (iv) angled or swirl injection methods. All these methods are currently being used by hybrid propulsion community to improve internal ballistics during the combustions.

6. Hybrid propulsion for Mars ascent vehicles

Mars Ascent Vehicle design concepts are studied by many researchers. Carter [21] discussed technology requirements for propulsion systems such as displacement pumps and bladder lined composite tanks. One of the experimental works for a potential MAV is presented by Karp with paraffin-based fuel and Mixed Oxides of Nitrogen (MON-3) oxidizer [22]. Furthermore, Evans and Karabeyoglu also studied MON based oxidizer for MAV experiment with metallized SP7 fuel by using 30 microns sized aluminum powder [23]. SP7 paraffin-based solid fuel is developed by Space Propulsion Group, Inc., specifically for this program.

This chapter proposes a classical hybrid propulsion system by using $Paraffin/Mg/CO_2/N_2O$ propellant combination is totally feasible for MAVs. Propellant combination provides significant cost savings as well as ease of manufacturing. Self-pressurizing capability of oxidizers also make the system simple and safe. Reduction in oxidizer to fuel ratio is another advantage of the system that reveals lighter oxidizer tank.

A hybrid rocket motor with a 38 bars combustion pressure, 98% of combustion efficiency, 3 kg/s of oxidizer mass flow rate and nozzle area ratio of 70 provides 250 seconds of specific impulse at an oxidizer to fuel ratio (O/F) of 1.1. Also, the thrust level of this single motor is found as 13 kN. Therefore, a potential Mars Sounding Rocket with total fuel mass of 40 kg have total oxidizer mass of 44 kg. Total propellant mass corresponds 84 kg. 1 kg payload mass is assumed to transfer a sample from a point to another on the Mars. Structure mass of the rocket is estimated as 18 kg consist of motor interface, motor casing, measurement devices and the oxidizer feed system (plumbing and valves). Avionics and power system is 5 kg. Nosecone is 2 kg.

The oxidizer tank mass is depending on the density of the oxidizer at 50 bars. It is worth to note that saturated oxidizer mixture at 50 bars need the tank temperature of 15°C. Mars atmospheric temperatures changing between -70 *and* 20°C near the equator. Thus, a heater system with a simple thermostat can be used at night times to increase the temperature to 15°C. On the other hand, launch can be performed in Martian summer days such as July or August.

At the 50 bars, CO_2/N_2O mixture has a liquid phase density of 816 kg/m^3. 44 kg of oxidizer makes 54 liters of oxidizer tank for the liquid phase. Therefore, tank mass with 4 mm thickness is 8.7 kg.

The sounding rocket has 17 seconds burn time and the mass ratio $\left(n = \frac{M_{initial}}{M_{final}}\right)$ of 4.8. 2-DOF calculation shows that rocket have 47 km downrange distance with 24 km burn out altitude. The maximum altitude achieved is 2 km. However, 3-DOF calculation is needed in order to increase the launch precision. The proposed rocket system can be scaled up as Mars Ascent Vehicle. By using the same performance parameters, ΔV of MAV system is found as 3850 m/s. In addition, ΔV requirement of 500 km low Martian orbit is found as 3652.3 m/s. It is worth to note that drag force is neglected since the calculation needs the drag coefficient. Drag coefficient will be analyzed in future study as the MAV trajectory design.

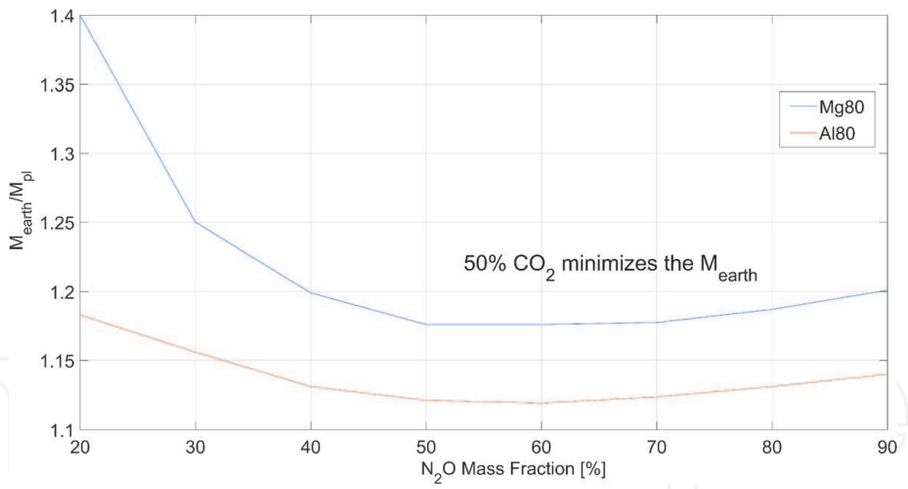

Figure 14.
Oxide formation after the motor experiment.

Potential MAV design needs at least two staged rocket design to fulfill 3652 m/s delta-V requirement. Because specific impulse of propellant selection is quite low for a single staged rocket. Thus, single staged rockets can be used for Mars ballistic hopper missions (such as Mars Sounding Rocket). In addition, oxidizer mass which is needed to brought from the Earth should be minimized for practical in-situ Mars sounding rocket. Considering a single staged hopper rocket with 1600 m/s reveals following minimization process. Eq. (5) is used for this minimization process.

$$\frac{M_{earth}}{M_{pl}} = \left[\frac{e^{\Delta V_{del}/Ispg_0} - 1}{1 - \epsilon e^{\Delta V_{del}/Ispg_0}}\right]\left[\epsilon + \left[\frac{1-\epsilon}{1+O/F}(1+\alpha O/F)\right]\right] \tag{5}$$

ϵ is the structural mass fraction. α is the nitrous oxide mass fraction in the oxidizer mixture. Nitrous mass fraction is the key parameter refers the earth based mass. O/F ratio is taken from CEA.

Earth based mass is minimized due to the payload mass. **Figure 14** summarizes minimized M_{earth}/M_{pl} due to nitrous oxide mass fraction for magnesium powder cases.

Although practical experiments are performed due to the Mg60 based fuel grains, Mg80 shows minimum mass fraction. Minimum values are taken at optimum O/F ratios. In addition, **Figure 14** shows minimum values both for Al80 and Mg80. Aluminum provides 5% smaller fraction than the magnesium. However, Al80 ignition with CO_2. is not practical.

7. Conclusion

This book chapter aims the explain the fundamentals of the hybrid propulsion system. In addition, readers can also be understand the practical setup configuration in hybrid rockets. Experimental tests are performed in order to understand the combustion characteristics of the carbon dioxide. Paraffin wax based fuel is the main binder. Aluminum and magnesium are selected as fuel additive. CO_2/N_2O mixture provides sustainable combustion mechanism.

This work concludes that $Paraffin/Mg/CO_2/N_2O$ is the most feasible propellant for Martian rockets. Carbon dioxide addition to the propellant reduces the oxidizer to fuel ratio. This means that Mars rockets can use lighter oxidizer tank. In-situ CO_2

significantly reduces the mass needed to brought from the Earth. Self-pressurizing feature of the CO_2/N_2O reduces complexity and the cost of the rocket. In addition, Mg/CO_2 combustion provides really high motor efficiencies. Hybrid rockets that uses in-situ based $Paraffin/Mg/CO_2/N_2O$ is the most prominent candidate due to several aspects such as low cost, safe launch operations, ease of manufacturing, and ease of design.

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Notes

This study is the brief version of the PhD Thesis presented by Ozan Kara at KOC University, Istanbul, Turkey. In addition, an extended version of this also found in AIAA Journal of Propulsion and Power.

Nomenclature

c_p	Heat capacity
E_{prop}	Released Energy (after the combustion)
I_{sp}	Specific Impulse
$M_{initial}$	Initial Rocket Mass
M_{final}	Final (burnout) Rocket Mass
n	Mass Ratio: Ratio of initial to final rocket masses
O/F	Oxidizer to Fuel Ratio
T_{comb}	Adiabatic Flame Temperature (Combustion Temperature)
T_{ref}	Reference temperature
T_{tank}	Tank Temperature, Oxidizer
P_{tank}	Tank Pressure, Oxidizer
χ	Mass Fraction
υ_{N_2O}	Specific Volume, Nitrous Oxide liquid phase
υ_{CO_2}	Specific Volume, Carbon dioxide liquid phase
$\overline{\upsilon}_{liquid}$	Average Specific Volume, liquid pha
ρ_{N_2O}	Density, Nitrous Oxide liquid phase
ρ_{CO_2}	Density, Carbon dioxide liquid phase
$\overline{\rho}_{liquid}$	Average Density, Liquid Phase
ΔH_f	Sensible Enthalpy
ΔV	delta V

Abbreviations

CAD	Computer Aided Design
CCP	Condensed Combustion Product
CEA	Chemical Equilibrium Analysis
DAQ	Data Acqusition
HEM	Homogeneous Equilibrium Model

HTPB	Hydroxyl-Terminated Polybutadiene
HTPE	Hydroxyl-terminated polyether
MAV	Mars Ascent Vehicle
MON	Mixed Oxides of Nitrogen
NASA	The National Aeronautics and Space Administration
PE	Polyethylene

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