

Effects of adding powdered metals with the solid propellants – A review

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Abstract. Rocket engines that use solid propellants are widely used in the commercial space flight industry for powering orbital-class launch vehicles and small research rockets. Thrust and the specific impulse developed by a rocket engine are essential properties of a rocket propulsion system, and it specifies the overall performance of a rocket. These properties heavily influenced by the burn-rate properties of the solid propellants. One of the many methods to improve the burn rate of the solid propellant is the addition of metallic powders into the fuel-oxidizer matrix. This technique has been observed to enhance the burn rate of the solid propellants; several studies have concluded the same. On the other hand, these additives result in the release of metal oxides into the atmosphere and lead to a higher amount of environmental pollution. This paper summarizes the effects of adding metals and their concentrations on the burning properties of the solid propellants.

1. Introduction

Burn rate of a solid propellant is an important parameter in determining the operational characteristics of a solid rocket motor. The burn rate of a propellant is highly influenced by the chamber pressure, the initial propellant temperature, oxidizer particle size, propellant composition, etc. Burn rate modifiers like metal powders, catalysts also have a significant influence on the burn rate. Several studies have been conducted on the effect of addition of such burn rate modifiers into solid propellants. Metals have been observed to enhance the burn rate of composite propellants by either reducing the decomposition temperature of the Ammonium perchlorate oxidizer or by lowering the activation energy (the initial energy required by propellant molecules to start the reaction). Burn rates are generally measured in a Crawford Burner: A Crawford burner is essentially a pressure vessel in which a propellant strand is placed with two fuse wires inserted into it, a time measurement is taken for the propellant to burn from one fuse wire to another, the pressure in the vessel is utilized to simulate the chamber pressure of a live burning rocket motor.

2. Literature Review

2.1. Size of Al Particles

2.1.1. Nano composites for solid rocket propellants



The paper focuses on the various components of the solid propellants like binder and aluminium for improving the ballistic performance of the powder. The effect of Al size and binder nature on the burning rates and residue oxide products of the propellants has been studied in this paper. Recordings from high speed video camera, burn rate measurements and residue analysis done by XPS, XRD and SEM are obtained for several propellants formulated, designed and manufactured at the laboratory. The propellant formulation is given in the table below:

Table.1 First series of propellant formulations tested [1]

Propellant	Al powder	Al powder nominal size (μm)	Binder
P_1	Alex	0.17	HTPB
P_1/x1	Alex	0.17	HTPB+KR12 disperdent
P_1/x2	Alex	0.17	PPG
P_5	Spheres	30	HTPB
P_1/b20	20% Alex 80% Flakes	0.17+50	HTPB
P_3/d20	20% Medium 80% Flakes	2.5+50	HTPB

Table.2 Second Series of propellant formulations tested [2]

Propellant	Al powder	Al powder nominal size (μm)	Binder
P_06/x1	μ -Flakes	50	HTPB
P_06/x2	μ -Flakes	50	PEG
P_06/x3	μ -Flakes	50	PEG
P_06/x4	μ -Flakes	50	PEG+double reticulant
P_06/x5	μ -Flakes	50	Peg(50%)/PPG(50%)

The propellant powders were burned in a nitrogen flushed window in order to measure steady burning rates under constant pressure. And it is observed that the solutions containing nanoparticles exhibit significantly higher burning rate

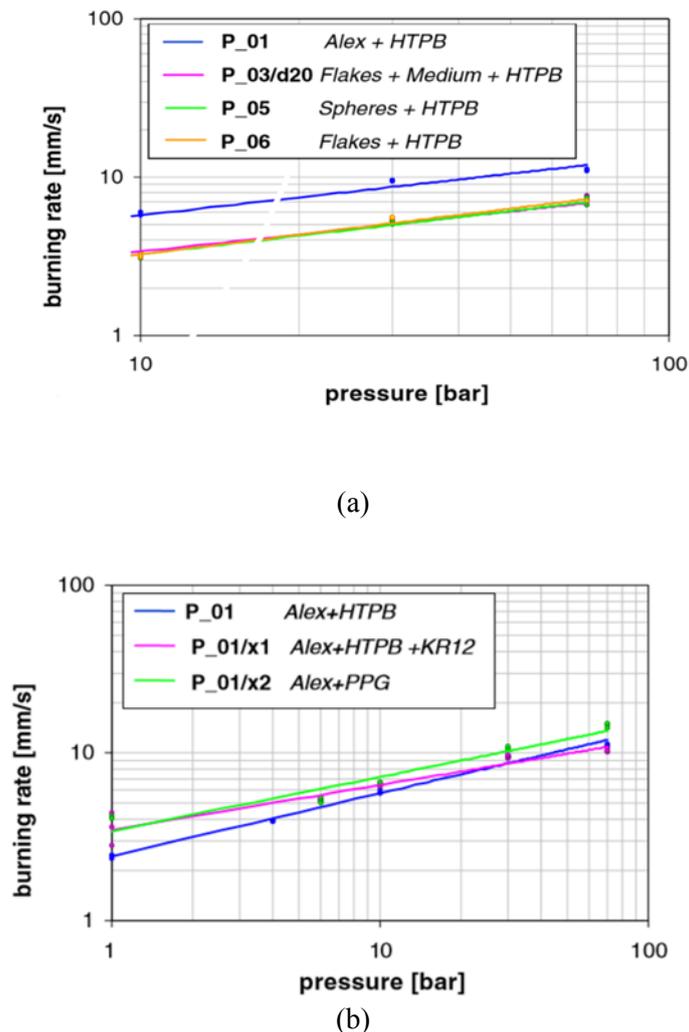


Figure.1 Burn Rate vs Pressure for (a) different aluminium particles (b) different binders [1]

The residue was collected into a pressurized Plexiglas vessel containing nitrogen and ice. It was later ignited using Ni-Cr wire. After combustion the residue is washed and treated with HCl. All the weights are normalised to the original weight of metallic Al present in the sample. The presence of metallic Al in the uncombusted fraction represented the incomplete burning process. XPS was used to measure the residue composition and the atomic concentration of chemical elements. The table below shows the atomic concentration data obtained at different pressures. Carbon is partially oxidised and comes from the pyrolysis process. Al is detected as Al oxide. The metallic Al is present within the core of agglomerates. Cl comes from the decomposition of AP and is also trapped within the agglomerates. XRD spectra data results are given in the table below: XRD crystalline fraction of combustion residues after treatment with HCL

Table.3 X-Ray Photoelectron Spectroscopy measurements of combustion products [1]

Propellant	Pressure(bar)	$\gamma\text{Al}_2\text{O}_3$	$\delta^*\text{Al}_2\text{O}_3$	$\alpha\text{-Al}_2\text{O}_3$
P_01	1	64.3%	33.4%	2.3%
P_01	30	53.9%	40.7%	5.4%
P_05	1	52.2%	32.6%	15.2%
P_05	30	60.3%	37.9%	1.8%

Table.4 X-Ray Diffraction measurements of combustion residue [1] XRD crystalline fraction of combustion residues

Propellant	Pressure(bar)	Al^0	$\gamma\text{Al}_2\text{O}_3$	$\delta^*\text{Al}_2\text{O}_3$	$\alpha\text{-Al}_2\text{O}_3$
P_01	1	3.6%	56.7%	37.4%	2.4%
P_01	30	1.5%	57.2%	37.7%	3.6%
P_05	1	71.9%	16.70%	9.0%	2.4%
P_05	30	9.8%	48.4%	40.0%	1.8%

The result is the low content of metals in the residue in the P_01 sample. It is inversely proportional to pressure. Thus, the smaller the Al powder, more is the burning. The SEM observations show that the size of combustion products depends on: size of Al powder, nature of binder and the burning pressure. It helped to establish a relationship between structure and chemical composition to ballistic properties. The burning rate was increased by two factors with the use of Nano-sized Al powder and PPG binder which easily degrades during the process of burning limiting the agglomeration of Al. Thus, resulting in efficient combustion.

2.1.2. Enhanced Propellant Combustion with Nanoparticles

The dependence of burn rate on the size of the aluminium powder particles was studied by varying the particle size from micrometre to nanometre scales. The study employed 15% Alex particles and aluminium nanoparticles produced by Technanogany, LLC. Both these additives were tested at varying particles size of the aluminium particle and then the following graph was plotted. It is evident that there is a sharp rise in the burn rate as the aluminium particle size is decreased to a nanometre scale. The burn rate seems to reach an inverse particle diameter squared dependence.

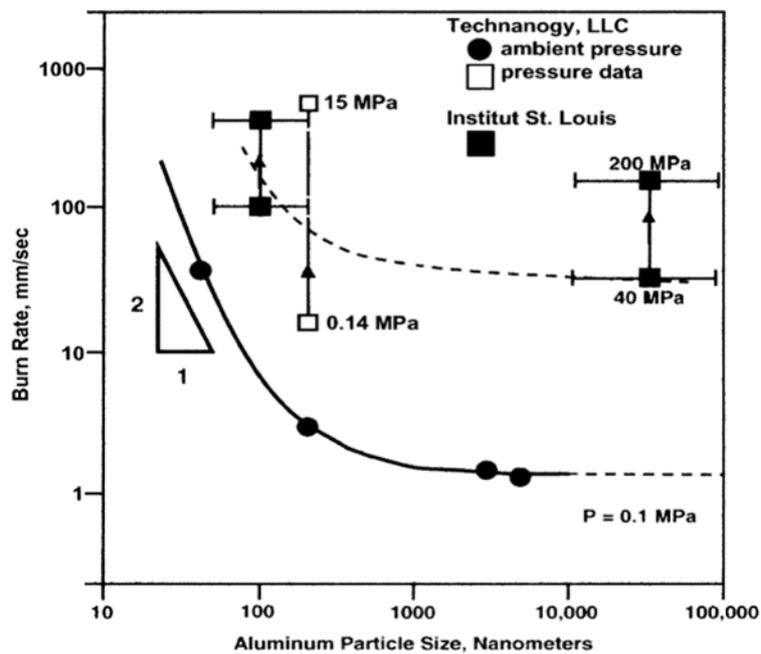


Figure.2 Variation of burn rate with aluminium particle size [2]

2.1.3. Combustion of HTPB-based solid fuels containing nano-sized energetic powder in a hybrid rocket motor.

The effect of addition of nano sized metal particles or Boron (B_4C) to solid HTPB fuel in a hybrid rocket motor is discussed. Nano sized particles were embedded into the solid fuel during the casting of the furl grain. A long grain centre perforated propellant grain was cast. It had already been demonstrated that addition of Alex particles into solid HTPB fuel can increase the fuel burn rate by up to 70%. It showed that an improvement in performance can be achieved by addition of aluminium powders. In addition to this, the production of finer WARP-1 aluminium powder with a much specific area which was also used.

Table.5 Propellant formulations used [3]

Solid fuel	Formulation (by weight %)	Density (g/cm^3)
SF1	100% HTPB	0.920
SF2	13% Alex [®] +87% HTPB	1.151
SF3	13% B_4C +87% HTPB	1.138
SF4	6.5% WARP-1+93.5% HTPB	1.036
SF5	6.5% B_4C +6.5% WARP-1+87% HTPB	1.144

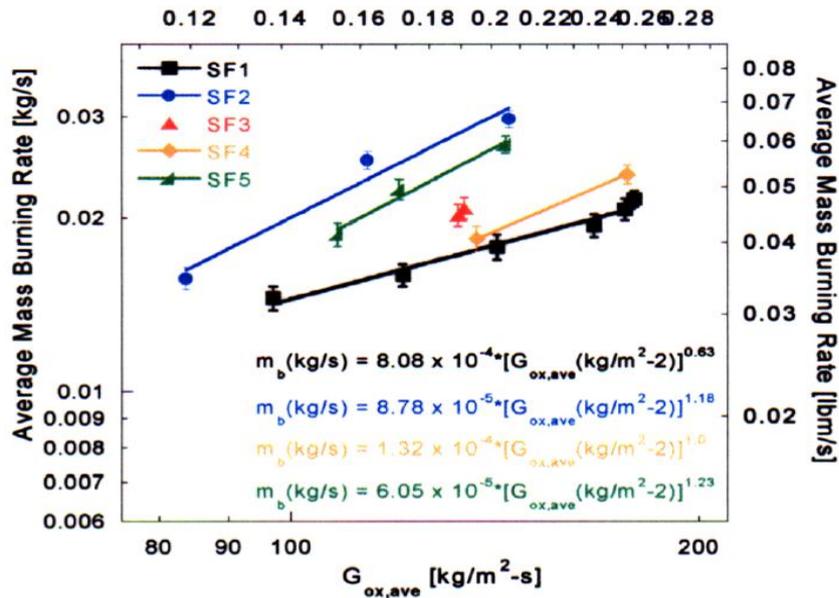


Figure.3 Variation of burn rate with oxidizer flow rate [3]

It can be seen that at the same oxidizer mass flux, addition of energetic particles enhances the burn rate of the fuel. Addition of just 6.5% of nano sized WARP-1 showed a significant increase in the burn rate of the propellant.

2.2. Pressure Dependence of Al

2.2.1. Development of Strand Burner Test by Using Aluminized AP/HTPB

The study focuses on the investigating the relationship between the burn rates of aluminised AP at low pressure. The aim is studying the burn rates of aluminised AP/HTPB propellant under varying pressure.

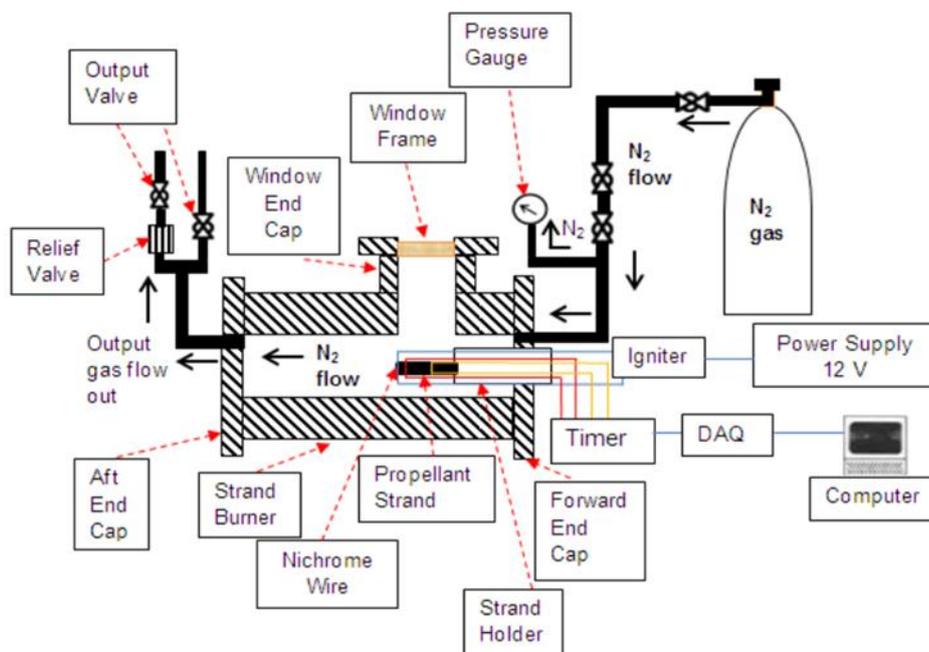


Figure.4 Schematic of the Crawford burner used [4]

The test is done under varying chamber pressure (1atm to 7atm in steps) using the strand burner, an apparatus for measuring the burn rates of solid propellants at increasing pressure. Then the plot is drawn for burn rate, r and the chamber pressure.

The same is done using a strand burner as mentioned above. There were four propellant formulations used for this test which contained AP, 5-micron Al with 85% solid loading and HTPB as the binder with 8-10% curing agent. The different formulations of these components used for the test are given in the table below.

Table.6 Propellant formulations tested [4]

Propellant	AP (%)	AL (%)	HTPB (%)	Oxidizer-Fuel ratio(O/F)
Formula 1	60	25	15	1.50
Formula 2	66	19	15	1.94
Formula 3	74	11	15	2.84
Formula 4	80	5	15	4.00

After the preliminary tests were run the tests under atmospheric conditions were conducted (by supplying air sans nitrogen) for each formulation. The same was repeated after filling the burner with nitrogen gas.

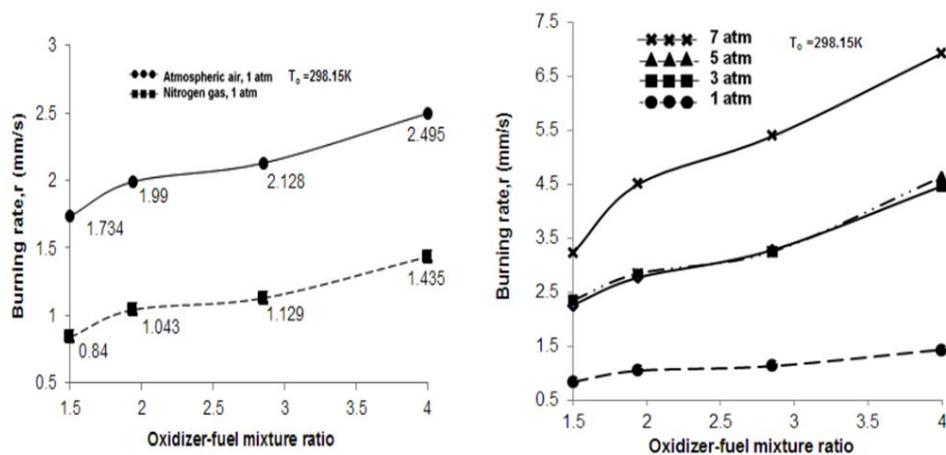


Figure.5 Burn rate variation with O/F ratio at different pressure [4]

Also, the tests were run by varying the chamber pressure from 1atm, 3atm, 5atm and 7atm in the nitrogen gas condition and the graph for the obtained data was plotted which showed that the burn rate was higher when the chamber pressure was increased. Thus, in conclusion, the paper says that the best and accurate way to conduct a burn rate test for varying formulations of the propellants is in an inert gas medium (like nitrogen). And it was found that the burn rate is directly proportional to the chamber pressure.

2.3.Addition of other metals

2.3.1. Burn rate enhancement of AP-NC solid propellant using CuO-graphene foam microstructures

The study focuses on experimentally enhancing the burn rate of the AP-NC solid propellant using CuO- graphene microstructures which are highly conductive, interconnected and porous. Here nitrocellulose acts as the binder. The authors made use of 3-D graphene foam with CuO as the metal

oxide instead of the conventional 2-D graphite support metal oxide- which showed no significant improvement. Here further exploration has been done on the catalytic property of 3-D graphene foam and its application to any kind of propellant irrespective of the chemical composition. The tests for burn rates of AP-NC with various CuO-graphene loadings, determining the effects of addition of CuO to GF and the activation energy of AP-NC were conducted using SEM, XPS, TG and DSC. The GF structures were grown on Ni templates using CVD techniques with a combination of three gases CH₄, H₂ and Ar at a temperature of 1050°C. Then they were functionalised with CuO using simple hydrothermal approach. The bonding between them was then investigated using XPS. In this study there was a difference of almost 20.3eV in the binding energy which confirmed the presence of CuO phase only. This was further confirmed using the XRD. Three samples of composite solid propellants were prepared: without GF and CuO, without GF but with CuO and with GF. For all the propellant samples burned they were ignited using a resistive Ni-Cr wire and a 10V DC voltage. The burn rates were measured tracking the brightest zones of the reaction zone as observed by the IR cameras. For pure AP-NC an average burn rate of 1.3±0.2 cm/s was obtained. But with addition of GF (around 25% loading) the average burn rates were 4.5 cm/s. With use of GF-supported CuO, burn rates up to 9 cm/s were obtained, which were 7 times that of the pure AP-NC burn rate. The positive effect came from the use of CuO acting as the catalyst, but the negative effect came from the fact that CuO was not taking part in the combustion thus, reducing the overall calorimetric value of the propellant. This indicated that there was an optimum CuO loading (~3%) which maximised the burn conditions. To determine the activation energies of the AP-NC propellants on addition of CuO-GF, TG and DSC analysis were performed. The activation energies were calculated using Kissinger method using 4 different heating rates along with HTD (High temperature decomposition) peaks. The analysis showed that the activation energy of AP-NC was lowered by 22% by addition of CuO-GF structures.

Table.7 Activation energies different propellant formulations [5] Calculated activation energy

Propellant type	GF loading (%)	CUO loading (%)	Activation energy (kJ/mol)
AP	0	0	126
AP-NC (70/30)	0	0	123
AP-NC+CuO	0	3	112
AP-NC+GF	10	0	123
AP-NC+GF-CuO	10	3	100
AP-NC+GF-CuO	10	8	96

This work presented a new approach of using 3-D GF with CuO catalyst for enhancing the burn rates and other characteristics of the solid propellants (AP-NC). The authors obtained a burn rate enhancement of 7% with 3% CuO loading for and 10% GF loading. Also, the AP-NC propellant samples with only the CuO nanoparticles at the same loading had 1.8% enhancement only. The GF-CuO structures not only enhance the transport of propellant but also gives an effective contact between propellant and CuO i.e., increase in catalytic effect.

2.3.2. The effect of Nd₂O₃ on thermal and ballistic properties of AP based composite propellants

The study was on the effects of Nd₂O₃ on the thermal and ballistic properties of AP based composite propellants. The composite propellants were prepared by slurry cast techniques using sigma blade

mixer. The ballistic parameters were determined by acoustic emission technique. The Nd₂O₃ which is a rare earth oxide and a p-type semiconductor was selected for this work. For the experiment the materials used were: AP crystals (200 micron ground to the size of $\sim 10 \pm 1$ micron), Nd₂O₃ (99.9% pure), propellant grade Al powder, HTPB and Dioctyle adipate (DOA). Using the slurry grade technique the propellant batch (weighing 2.5kg each) was prepared. Burn rate determined by acoustic emission technique for both Nd₂O₃ based and Fe₂O₃ formulation revealed the results tabulated below

Table.8 Burn rate coefficient and pressure index of Nd₂O₃ and Fe₂O₃ [6]

Sr.no	Batch	30-50 kg/cm ²		50-70 kg/cm ²		70-125 kg/cm ²		Density (g/cc)
		a	η	a	η	a	η	
1	EWP-002 based on Nd ₂ O ₃	1.26	0.5	2.57	0.27	0.54	0.64	1.75/1.74
2	EWP-003 based on Fe ₂ O ₃	1.15	0.04	2.23	0.23	2.06	0.34	1.74/1.74

Nd₂O₃ gives a typical burn pattern. In the pressure range of 50-70 kg/cm² the pressure index for Nd₂O₃ based formulation is lower than that of Fe₂O₃ based formulation. But in the pressure range of 70-125 kg/cm² the scenario is reversed which is both beneficial and unique when compared with Fe₂O₃. The impact and sensitivity tests showed that the Nd₂O₃ based formulations were less sensitive than compared to Fe₂O₃. Thus, the study reveals that Nd₂O₃ appears to offer high potential to the propellants for specific applications.

2.4. An effective method to embed catalyst on AP and its effect on the burn rates of aluminized composite solid propellants.

A study aimed at learning the effect of embedding an Iron Oxide catalyst on the surface of Ammonium Perchlorate oxidizer in a solid AP/HTPB propellant [4]. Micro and Nano sized catalyst was embedded into the propellant grain and then burn rate measurements were made on a Crawford burner test rig. The results of the Crawford burner test for the micron sized Iron Oxide are as follows: List of various composition prepared for optimum IO fraction in aluminized solid propellant

Table.9 Different propellant formulations used [7]

Mix No	AP%	Al%	IO%	Binder%	Density obtained (theoretical) (kg/m ³)
c1	68	18	0	14	1760 (1777)
c2	67.5	18	0.5	14	1763 (1771)
c3	67	18	1	14	1768 (1787)
c4	66.5	18	1.5	14	1781 (1792)

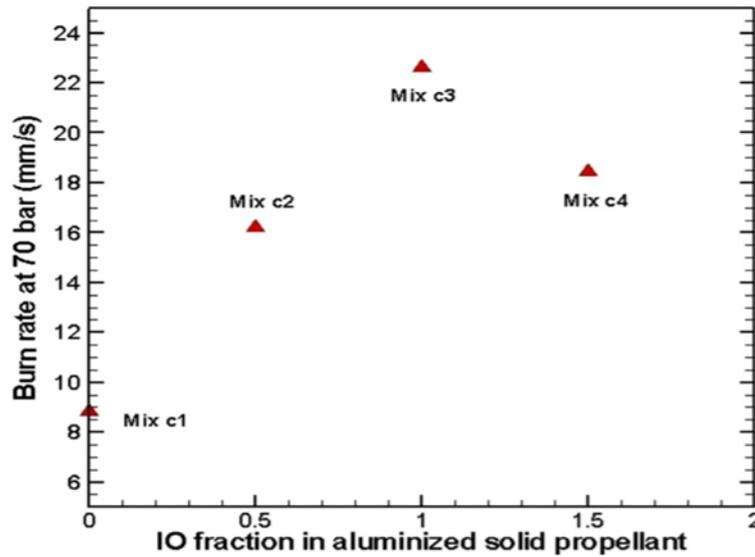


Figure.6 Variation of burn rate with Iron Oxide content [7]

After observing that the burn rate peaks at 1% Iron Oxide, further investigation was done, leading to the following propellant formulations

Table.10 Propellant mixtures with 1% Iron Oxide [7]

Mix No	AP%	AL%	IO%	Binder%	Density obtained (theoretical) (kg/m ³)	End viscosity (poise)
1	68	18	0	14	1760 (1777)	3.23*10 ³
2	67	18	1	14	1768 (1787)	3.51*10 ³
3	67	18	1	14	1771 (1780)	3.36*10 ³
4	67	18	1	14	1765 (1787)	4.27*10 ³
5	67	18	1	14	1769 (1787)	3.79*10 ³

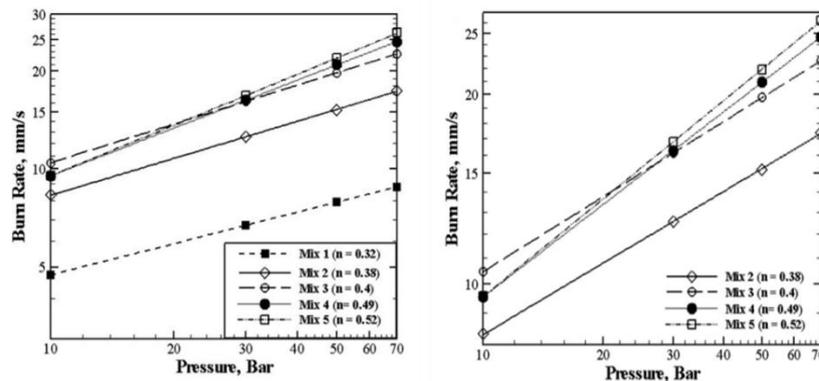


Figure.7 Variation of burn rate with Chamber Pressure [7]

2.5. Mechanism of Burning rate enhancement of composite solid propellants by Ferric Oxide:

By adding limited amount of ballistic modifiers to the propellant formulation, the burning rate of the composite solid rocket propellants like ammonium perchlorate is adjusted. The most common catalyst for increasing the burning rate is iron oxide (IO, Fe₂O₃). This paper studies about the combustion mechanisms of solid propellants using sandwich-burning method. By this method we can observe and characterize the combustion behaviour and it can easily vary the test samples and its preparation. This study concerns combustion with various iron catalysts and oxidizers in the binder lamina. In this experiment, there are three techniques are taken to study that is combustion videography, examination of quenched samples in the scanning electron microscope (SEM) and hot-stage (optical) microscopy (HSM) of ingredients.

Table.11 Binders used in this study [8]

No	Binder%	Prepolymer%	Plasticizer %, (DOA)	Curing Agent	
				Type	Amount %
1	PBAN	64.14	15.00	ECA	20.86
2	HTPB-DDI	69.07	16.77	DDI	14.16
3	HTPB-IPDI	75.73	18.39	IPDI	5.88

In the above table 10, there are three different binder types and its compositions. HTPB-IPDI and HTPB-DDI are used to denote HTPB cured by isophorone di-isocyanate (IPDI) and dimeryl di-isocyanate (DDI) respectively. Effect of oxidizer type, susceptibility of the binder to melt flow, AP particle size and dispersibility of the catalyst have been observed during the study.

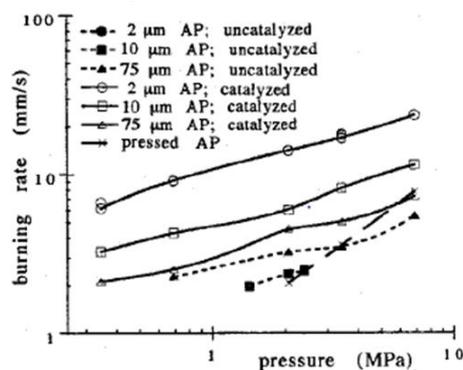


Figure.8 Burn rate vs pressure for different propellant formulations [8]

There is an increase in burning rate by the Fe₂O₃ catalyst in AP/hydrocarbon binder propellants that may act as multiple paths. The fine particulate oxidizer filled matrices shows that catalyst enhances exothermic reactions that is very close to the surface along the oxidizer-binder contact lines. The heat release and reactive fuel and oxidizer species are important for these reactions as the density will increase with decreasing AP particle size for the contact lines and the proportion of AP will also increase in the AP or binder matrix

3. Environmental aspect of burn rate enhancers

Most techniques of burn rate enhancement involve addition of either a metal or metal oxide into the propellant matrix. When burned, these propellants release oxides of these metals into the atmosphere where these metal oxide particles might get suspended and turn into particulate matter. Particulate matter is a significant part of the pollutants in the atmosphere, it blocks the sunlight from reaching the earth's surface, it might get accumulated on leaves, essentially restricting the plants' respiration. It also reduces visibility which can create a big number of its own problems.

4. Conclusion

Addition of metals into solid rocket propellants results a significant increase in the burn rate which further leads to higher thrust and higher specific impulse. It is because the particle cause reduction in the decomposition temperature of ammonium perchlorate and also act as catalyst by increasing the surface area available for combustion. On the other hand, the exhaust from rocket motors with these propellants can have a strong negative impact on the environment. Therefore, more research needs to be done on more environment friendly materials that can be used to enhance the performance of solid rocket propellants.

5. References

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