Pressure Dependence, Propellant Composition, Particle Size & Effect of Catalyst on Burn Rate Study of AP-HTPB, AP- PVC & AN-HTPB based Compo-Site Solid Propellants

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Abstract— In the present investigation, an effort has been made to study pressure dependence, propellant composition, particle size and effect of catalyst on the burn rate of AP and AN based composite solid propellant. The variation of oxidizer has been made 70%, 75% and 80% based on earlier experience of the loading of PVC and HTPB on the physical and combustion characteristics of AP and AN based composite solid propellants. The particle size of the oxidizer in the present formulation is taken to be 44 µm and 149 µm respectively. The bimodal AP and AN are taken with mess size 150 and 300.The reason for taking this formulation is to compare the burning rate of the selected propellant and hence finding the best propellant.

Key words: Burn Rate; AP-HTPB; AP- PVC; AN-HTPB; Fe_2O_3

I. Introduction

The burning of solid propellants occurs in a very thin region at a surface of the charge. Some of the heat from the burning gas is transferred into the charge, raising its temperature. There is a temperature gradient through the charge, the temperature adjacent to the burning surface being that of the burning gas (flame temperature), and the temperature at some distance inside the charge being that at which the charge was before the motor was fired. As burning proceeds and the burning surface recedes into the charge, at some fixed point in the charge the temperature rises. The propellant softens and melts. This decomposes the gases, which react chemically and ignite, burning at the flame temperature. Meanwhile, the propellant at some point has begun to soften and will go through the same reactions. Thus burning continues, and the burning surface recedes steadily into the charge. The burning surface regresses by burning in parallel layer in a direction perpendicular to the surface itself. The rate at which the surface regresses due to burning or the rate at which the flame front propagates to the free surface of the grain is called the "linear burning rate" of the propellant.

The burning rate of solid propellant depend on various parameters i.e, Chamber pressure, Initial temperature of the propellant, Gas velocity of hot combustion products over the burning surface, Chemical formulation, Oxidizer-binder mixture ratio, Oxidizer particle size (for composite propellants), Total mass flow rate over the burning surface. Some other factors which affect the burning rate are catalysis, sub atmospheric combustion, erosion, radiation, acoustics, electrical fields, and acceleration and surface effects.

A. Dependence of burn rate on Pressure

The burning rate dependence on pressure can be expressed as

$$r = a * P_c^{\ n} \qquad \text{(Equation 1)}$$

This is known as De Ville's or St. Robert's law. This happens to be very accurate for all types of propellant and is generally used. In this expression 'n' called the pressure exponent or the combustion index is essentially independent of the initial grain temperature but describes the influence of rocket chamber pressure on burning rate. The other constant 'a' called temperature coefficient is influenced by ambient temperature.

B. Dependence of Burn Rate on Propellant Composition

Propellant composition has a marked influence on the burning rate. All attempts have so far converged in the search of high performance propellants, and they concluded that the burning rate increases with the increase in percentage of oxidizer but only upto a certain limit.

C. Dependence of Burn Rate on Particle Size

The performances of composite propellants have been shown to be directly proportional to the oxidizer content and particle size. The particle size of the oxidizer in the present formulation is taken to be 44 µm and 149 µm respectively.

Renie have investigated the effect of oxidizer size and distribution on non- aluminized composite propellants. They used a new mathematical model called as 'petite ensemble model'. They showed that the oxidizer particle size and distribution have profound influence on burning rate, pressure exponent 'n' and temperature sensitivity. They also showed that the combustion parameters were strongly dependent on coarse-to-fine and the mean diameter of the fine fraction.

D. Dependence of Burn Rate on Effects of Catalyst

The catalytic effect in certain materials has long been noted in solid propellants. A catalyst is a material that increases the reaction rate of a chemical reaction but remains unchanged at the end of the chemical reaction. Ferric oxide (Fe_2O_3) is taken as the catalyst in the present formulation.

II. Experimental

In the present work, it has been attempted to use AP - HTPB, AP - PVC and AN - HTPB composite solid propellant and study their combustion aspects. Three different composition were used for experimentally studies with prior experience of the mechanical and combustion behavior of AP - HTPB, AP - PVC and AN - HTPB propellant at the laboratory. The bimodal AP is taken with mess size 150 and 300. The AP are loaded at 70, 75 and 80 percents by weight in PVC plastisol processed with equal amount of DBP plasticizer. Similarly, the AP are loaded at 70,75 and 80 percents by weight in HTPB processed with DOA as plasticizer, TDI as curing agent and glycerol. Similarly ,the AN are loaded at 70, 75 and 80 percents by weight in HTPB processed with DOA as plasticizer, TDI as curing agent and glycerol. The basic formulations of the samples consisted of AP - HTPB +

catalyst, AN - HTPB + catalyst and AP - PVC + catalyst are shown in Table 1, 2 and 3.

A. Mixing of Ingredients

All the ingredients selected for above compositions were stored under 45% controlled humidity conditions. The processing variables, like mixing time of one hour, mixer temperature 20°C - 25°C and sequence of ingredient addition into the mixer were kept similar in all the mixings. The quantities of PVC and DBP were mixed in a stainless steel vessel. The metal in a quantity of 3% of total ingredient by weight has been added subsequently for the metalized compositions. The mixing was done for 30 minutes to get the final mix. Altogether five such operations have been carried out to get the same number of compositions.

B. Casting of Propellants Slurry

The slurry was cast in plastic mould which were cleaned and greased with Metroark grease beforehand to ensure that the surface of the propellant would be smooth and flat without any rough patches.

C. Curing

The propellant slurry filled plastic containers were kept in a vacuum electric oven at 60 ^{0}C ± 2 ^{0}C for a period of six days to allow it to cure. The moulds were then removed from the oven and allowed to cool to room temperature. The propellant samples were stored in polythene bag and then into a desiccators to avoid moisture absorption.

S.No	AP (wt%)	HTPB (wt%)	DOA (wt%)	TDI (wt%)	Glycerol (wt%)	Fe_2o_3 (wt%)
1	70	21.59	6.48	1.70	0.23	-
2	75	17.99	5.40	1.42	0.19	-
3	80	14.39	4.33	1.13	0.15	-
4	70	21.59	6.48	1.70	0.23	3
5	75	17.99	5.40	1.42	0.19	3
6	80	14.39	4.33	1.13	0.15	3

Table 1: Composition of AP-HTPB Samples

S.No	AN (wt%)	HTPB (wt%)	DoA (wt%)	TDI (wt%)	Glycerol (wt%)	Fe_2o_3 (wt%)
1	70	21.59	6.48	1.70	0.23	-
2	75	17.99	5.40	1.42	0.19	-
3	80	14.39	4.33	1.13	0.15	-
4	70	21.59	6.48	1.70	0.23	3
5	75	17.99	5.40	1.42	0.19	3
6	80	14.39	4.33	1.13	0.15	3

Table 2: Composition of AN-HTPB Samples

Sr. No	AP (% wt)	PVC (% wt)	DBP (% wt)	Fe_2O_3 (% wt)
01	70	15	15	-
02	70	15	15	3
03	75	12.5	12.5	-
04	75	12.5	12.5	3
05	80	10	10	-

Table 3: Composition of AP-PVC Samples

III. EXPERIMENTAL

A. Burning Rate Studies

The burning rates of AP - HTPB, AP - PVC and AN - HTPB with and without catalyst propellants were determined at ambient condition and different pressures, 2.06, 4.76 and 6.89 MPa, using a conventional strand burner. Nitrogen gas was used to pressurize the bomb. The dial type pressure gauges were used to record incoming pressure and pressures in bomb and line. A surge tank was provided in the set - up to ensure that a strict pressure level is maintained in the bomb represent the systematic diagram and line diagram of high pressure strand burner apparatus. This has been shown clearly in Fig. 1 and Fig. 2.

The propellant strands, having two fine drilled holes at a distance of 5cm to position the fuse wires, were installed in the bomb and igniter wire was suitably placed at apex of the strand. The cap with the provision for electrical connections in it was tightened on to the bomb. The bomb was then pressurized with nitrogen gas to required pressure level. The necessary electrical connections were made and all strands were ignited to record time with the help of an electrical timer. The burning rates were then determined by averaging the three close readings for each case.

Fig. 1: High Pressure Strand Burner setup

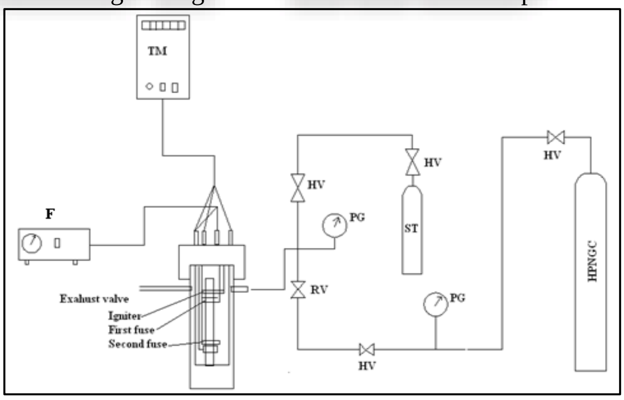

Fig. 2: Line diagram of High Pressure Strand Burner*where HV - Hand valve, RV - Regulating valve, PG - Pressure valve, ST - Surge tank, F-Firing unit , TM - Timer, HPNGC - High pressure nitrogen gas cylinder

IV. RESULTS & DISCUSSION

The burning rate measurements were obtained by using high pressure strand burner at 2.068, 4.765 and 6.895 MPa in the presence of nitrogen atmosphere. It is well known that the transition metal oxide affects decomposition and combustion behavior of composite solid propellants and catalytic activity of metal oxide is dependent on catalyst concentration and surface area. It is also believed that the catalyst being very stable in nature influence the gas phase combustion process at high temperature and pressure. Therefore, this study is directed to assess the effectiveness of Ferric oxide (Fe_2O_3) on the combustion behavior of the ammonium perchlorate (AP) and ammonium nitrate (AN) oxidized loading with different composition of hydroxyl terminated polybutadiene (HTPB) and polyvinyl choride (PVC) based composite solid propellants.

A. Burn Rate Studies of with & without Catalyst AP- HTPB Composite Solid Propellants

The burning rate measurements were carefully carried out by using strand burner at 2.068, 4.765 and 6.895 MPa by pressurizing nitrogen gas. The pressure dependence of burning rate of AP - HTPB has been shown in table 4 and 5. It is found from that the burning rate of propellant containing 80% AP loading have been found to be higher than the corresponding propellants of 75% and 70% AP loading (figure 3). At ambient pressure the burning rate of the composite solid propellants are increasing as the AP loading is increases. But as the 3% ferric oxide is added in same compositions it gives high burn rate at 70% AP loading as compare to others AP - HTPB based composite solid propellants. The experiment is conducted on 2.068, 4.765 and 6.895 MPa pressure. The burning rate increases with increase in pressure and 80% AP - HTPB based composite solid propellants with ferric oxide (figure 3) shows drastic variation from 9.250 to 44.407 mm sec^{-1} at 1000 psi chamber pressure. As the preparation is very difficult for 80% AP - HTPB based composite solid propellants with and without ferric oxide, which gives higher value of pressure index i.e. 0.526. The temperature coefficient is minimum in75% which shows lowest performance with respect to the others. A comparative graph has been plotted in figure 3.

The burning rate of the propellant is found to increase with combustion chamber pressure. The increase in the rate of burning with pressure may be attributed to the more contribution of reaction kinetics process of controlling of burning rate when compared with diffusion controlled process at high pressures.

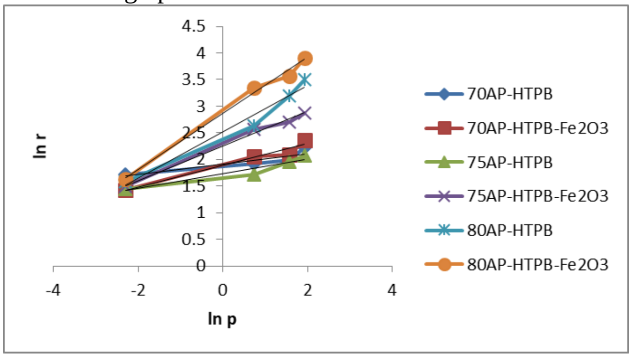

Fig. 3: Comparison of STA graph showing DSC/TG of AP - HTPB composite solid propellant

Types of Propellant	Burning Rate (mm sec^{-1}) Pressure (MPa) 0.101 4.760 2.068 6.895				a	n
70% AP-HTPB	4.16	6.76	7.26	9.25	6.2	.098
70% AP-HTPB with 3% Fe_2O_3	5.55	7.87	8.13	10.63	6.7	.203
75% AP-HTPB	4.26	5.54	7.02	7.96	5.02	.136
75% AP - HTPB with 3% Fe_2O_3	4.44	13.04	14.91	17.54	10.31	.323
80% AP - HTPB	4.87	13.97	24.58	33.31	10.19	.433
80% AP - HTPB with 3% Fe_2O_3	5.12	28.2	35.68	44.40	19.24	.52

Table 4: Burn Rate Studies of Catalyzed & Uncatalyzed AP-HTPB based Composite Solid Propellant

Types of Propellant	ln r ln p -2.2920 0.7265 1.560 1.9307				ln a	n
70% AP - HTPB	1.713	1.916	1.982	2.224	1.829	0.098
70% AP - HTPB with 3% Fe_2O_3	1.426	2.063	2.095	2.364	1.915	0.203
75% AP - HTPB	1.450	1.713	1.949	2.074	1.613	0.136
75% AP - HTPB with 3% Fe_2O_3	1.490	2.568	2.702	2.864	2.333	0.323
80% AP - HTPB	1.584	2.636	3.202	3.496	2.322	0.433
80% AP - HTPB with 3% Fe_2O_3	1.633	3.339	3.574	3.900	2.956	0.526

Table 5: Pressure Dependence of Burning rate of AP - HTPB based Composite Solid Propellants at different Pressure

B. Burn Rate Studies of with and without catalyst AN- HTPB Composite Solid Propellants

At the same pressure variation when the experiment is taken out with ammonium nitrate in place of ammonium perchlorate, it is found that none of the propellants burn satisfactorily at 2.0685 MPa nitrogen pressure in the strand burner. Hence, these data are not considered in the present analysis. In open atmosphere, all the propellants burn when ignited with the help of an ignition device. Also, 70% AN - HTPB based composite solid propellants with and without catalyst shows no effect of burning at high pressure upto 6.895 MPa. The burning rate of the propellant is presented in Table 6 and 7 shows similar results for all the compositions with ± 0.3 variation upto 6.895 MPa. The burning in open atmosphere may be attributed to the participation of atmospheric oxygen in the combustion processes of the propellants. At atmospheric condition it leaves carbon skeleton after completion of burning with huge smoke. Ammonium nitrate is more sensitive than the Ammonium perchlorate as it absorb moisture, if it is kept in open space and very difficult to remove moisture easily from it. This gives the reason for its poor performance and it results negative values of temperature coefficient shown in figure 4. It is observed that incorporation of catalyst increases the burning rate of AN - HTPB propellant at all pressures. However increases in burning rate due to addition of catalyst depends on the nature of catalyst incorporated. A comparison of burn rate of AN-HTPB composite solid propellant with variation in pressure is shown in figure 4.

Types of Propellant	Burning Rate (mm sec^{-1}) Pressure (MPa) 0.101	4.760	2.068	6.895	a	n
70% AN - HTPB	0.167	-	-	-	-	-
70% AN - HTPB with 3% Fe_2O_3	0.187	-	-	-	-	-
75% AN - HTPB	0.196	-	1.88	2.428	0.750	0.588
75% AN - HTPB with 3% Fe_2O_3	0.232	-	2.062	2.690	0.849	0.568
80% AN - HTPB	0.238	-	2.061	2.365	0.871	0.551
80% AN - HTPB with 3% Fe_2O_3	0.416	-	2.257	2.481	1.212	0.398

Table 6: Burn Rate Studies of Catalyzed and Uncatalysed AN-HTPB based Composite Solid Propellant

Types of Propellant	ln r ln p -2.2920	0.7265	1.560	1.9307	ln a	n
70% AN - HTPB	0.167	-	-	-	-	-
70% AN - HTPB with 3% Fe_2O_3	0.187	-	-	-	-	-
75% AN - HTPB	0.196	-	1.88	2.428	0.750	0.588
75% AN - HTPB with 3% Fe_2O_3	0.232	-	2.062	2.690	0.849	0.568
80% AN - HTPB	0.238	-	2.061	2.365	0.871	0.551
80% AN - HTPB with 3% Fe_2O_3	0.416	-	2.257	2.481	1.212	0.398

Table 7: Pressure Dependence of Burning Rate of AN- HTPB based Composite Solid Propellants at Different Pressure

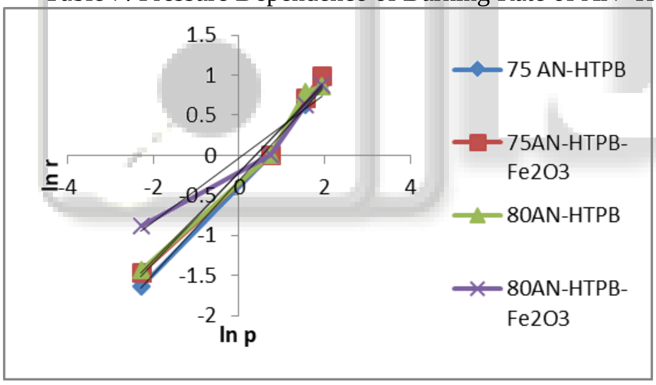

Fig. 4: Comparison of burning rate 70, 75 and 80% of AN-HTPB Composite Solid Propellant with Catalyst

C. Burn Rate Studies of with & without catalyst AP- PVC Composite Solid Propellants

The burning rate for 70, 75 and 80% AP and remaining constituents of PVC and DBP has been explained in Table 3. The nature of the plots in all the cases is identical and the burning rate is found to increase in the combustion chamber by varying nitrogen gas at similar pressure which is used previously.

The increase in the burning rate may therefore be viewed as directly because of its dependence on the combustion pressure in each case. The increase in oxidizer loading also increases the burning rate. The main emphasis has been put in the present investigation is higher loading of AP i.e. 80 wt% does not sustained, which shows brittle nature is not applicable for experimental work.

At 0.101 MPa almost all propellants gives same burning rate i.e. 2.010±0.1. but the result changes with increase in pressure from 5.810 to 9.891 mm sec^{-1} upto 6.895 MPa. The highest pressure shows high burning rate and it also dependent on higher loading. 75% and 80% oxidized loading gives higher burning rate with high combustion index 0.376.

The nature of the plots in all the cases is identical and the burning rate is found to be increase with combustion pressure. On comparing the three set of burning rate data obtained in the figure 3, 4 and 5, when the AP and AN loading increased in the propellant, the burning rate, as also the nominal combustion pressure increases. The increase of AP loading ensures the combustion reaction to reach its completion and even the burning surface temperature and rate of condensed phase reactions may be taken have increased, not to say that the gas phase reactions and the heat in flux to the burning surface would definitely increase.

It is observed that incorporation of Fe_2O_3 as a catalyst increases the burning rate of AP-PVC propellants at all pressures. However increases in burning rate due to addition of catalyst depends on the nature of catalyst incorporated.

The results tabulated in Table 4 to 9 shows that the effect of Fe_2O_3 on burning rate of AP and AN propellants system at different pressure levels i.e. from ambient (0.101) to high pressure (at 2.068, 4.76 and 6.895 MPa) as well as propellants with 3 wt % concentration of catalyst are compared. An exponential dependence of burning rate on pressure is observed in accordance with the well-known Ville's law. The results show (figure 3,4 and 5) that the burning rate of uncatalysed AP-HTPB propellants at different pressures is similar to values mentioned in literature no. Analyzing the burning rate of uncatalyzed and catalyzed propellants, it is observed that on adding Fe_2O_3, burning rate increases significantly in the following order:

HTPB - AN with 3 % Fe_2O_3 < AP - PVC with 3% Fe_2O_3 < HTPB - AP with 3 % Fe_2O_3

The burn rate results for various catalyzed composite solid propellants at different operating pressures. It can be noted that burning rate of AP-HTPB propellant with Fe_2O_3 is higher in comparison to other systems like AN-HTPB and AP-PVC propellant with ferric oxide. It can, thus, be seen that the propellant formulations studied in the present work promises to deliver the highest burn rate achievable with AP-HTPB propellant system.

Types of Propellant	Burning Rate (mm sec^{-1}) Pressure (MPa) 0.101 4.760 2.068 6.895				a	n
70% AP - PVC	1.89	5.810	6.172	6.410	4.66	0.301
70% AP - PVC with 3% Fe_2O_3	2.20	7.352	7.64	7.93	5.84	0.316
75% AP - PVC	2.010	6.03	6.261	6.626	4.87	0.292
75% AP - PVC with 3% Fe_2O_3	2.101	7.66	8.163	9.216	5.91	0.356
80% AP - PVC	2.164	8.62	9.619	9.89	6.55	0.376

Table 8: Burn Rate Studies of Catalyzed & Uncatalysed AP-PVC based Composite Solid Propellant

Types of Propellant	ln r ln p -2.2920 0.7265 1.560 1.9307				ln a	n
70% AP - PVC	0.637	1.759	1.820	1.857	1.539	0.301
70% AP - PVC with 3% Fe_2O_3	0.791	1.994	2.033	2.070	1.764	0.316
75% AP - PVC	0.698	1.796	1.834	1.891	1.583	0.2927
75% AP - PVC with 3% Fe_2O_3	0.742	2.036	2.099	2.220	1.776	0.356
80% AP - PVC	0.771	2.154	2.263	2.291	1.879	0.376

Table 9: Pressure dependence of Burning rate of AP- PVC based Composite Solid Propellants at different Pressure

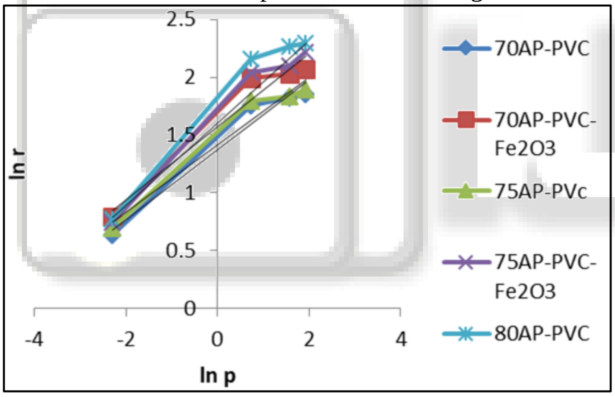

Fig. 5: Comparison of Burning Rate 70, 75 and 80% of AP-PVC Composite Solid Propellant with Catalyst

V. CONCLUSIONS

1) The burning rate of AP - HTPB composite solid propellants results very impressive data with expected combustion index values.
2) It was observed that the burning rate increases with increase of chamber pressure and also, the combustion pressure rate increases with increase in oxidizer loading for all the cases. Further, the phase transition, melting and decomposition processes of the oxidizer are pressure sensitive and associated peaks register a positive temperature shift with pressure.
3) Conversely, the addition of catalyst with 3 wt% ferric oxide especially in high pressure region shows drastic increase in burning rate with increase in AP % loading.
4) AN - HTPB based composite solid propellants are both hard to ignite and difficult to sustain combustion at ambient as well as high pressures. However, once ignited they burn smoothly at pressure around 4.765 Mpa. Finally, it is observed that the burning rate of AN - HTPB comes in lower side and the pressure index at higher side, indicate poor performance of the propellants.
5) Similar trend has been found for AP - PVC based propellants as observed in AP - HTPB based propellants with slightly lower data result.

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