Effect of catalysts on the burning rate of phase stabilized ammonium nitrate based composite propellants

Praveen Kumar1, Manish Kumar2, Rajan Lakra3
Space Engineering Rocketry (BIT Mesra)

Abstract. The Ammonium Nitrate based composite propellants are widely used in the applications of tactical missiles and explosives due to its least toxicity and smokeless combustion. The main disadvantage of ammonium nitrate based propellants is its poor burning rate. Hence, it is required to enhance its burning rate for attaining a better performance. One of the several methods of upgrade the burning rate of composite solid propellants is the addition of catalysts to the propellant. The present study aims to investigate the effect of addition of transition metal oxides as the catalysts to the phase-stabilized ammonium nitrate based composite solid propellants and to study its thermal decomposition characteristics.

1. Introduction

Ammonium nitrate (AN) has a large number of applications as a fertilizer and a component of a variety of energetic compositions as well, mainly industrial explosives. Another use of AN is also as an oxidizer in propellant formulations, but not to a very large extent as in explosive compositions. AN is absorptive, content of energy is rather below average, exhibits a lot crystalline phase transitions at normal usage temperatures, and endows AN-based propellants with a restricted range of burning rates. For the same reasons, the main AN use is in gas generators and other auxiliary power sources. However, AN is very economic, easily available, and safe energetic material which can be phase stabilized. It is environmentally friendly and generates smokeless combustion products, which is a very important characteristic that makes it a novel candidate oxidizer to decrease atmospheric pollution. The present need for virtuous propellants which can satisfy the high demand for automobile air bag systems gives rise to a new interest in AN combustion studies. Makoto Kohga reported that burning characteristics of AN-based composite propellants is enhanced by ammonium dichromate. The transition metal compounds have the ability of elevating the burn rate and ignitability of AN propellants. Both the theoretical adiabatic flame temperature and the specific impulse were increased by increasing the amount of ammonium dichromate (ADC).

1.1 Phase Transitions of Ammonium Nitrate

C.Oommen2 studied about ammonium nitrate thermal decomposition. It is known that at least five different polymorphic forms of AN are present at atmospheric pressure, with the correspondent transition temperature as follows:

The mechanical strength of the AN prills depends on the phase transition deportment. The technical significance attached to the thermal transitions is a key reason for the considerable literature available for the same. Lot of theory on the phase transformation bases the generally used idea that the mechanical strength of the prill must be related to the AN (IV) – AN (III). Polymorphic transition at 32°C which is led by a reasonable volume change (3.8%). AN prill is a polymorphic entirety. The change of volume of the elementary cell leads a change in the crystal packing in the polycrystalline
aggregate and subsequently, the adherence between crystallite reduces. The product mechanical strength thus reduces after a lot of thermal cycles through the transition temperature and the granular product becomes dust or fine particles, and enlarge the caking propensity.

The volumetric changes in regards with the phase change may lead to cracks in the propellant grain. These cracks in a propellant grain are undesirable as they can lead to catastrophic burning result. It is of vital importance to know the phase transition fully and modify it accordingly to make the salt fit for reliable practical use.

An observation of the stabilizing effect of KF is mainly due to the relatively low amount of KF compared to the other phase modifiers like potassium nitrate, which is required for phase modification. It is recommended that 1% by weight of KF can subdue the phase transition of AN entirely.

1.2 Burning of Composite Propellants with Catalyst
E.W. Price14 reported the effect of titanium dioxide on a HTPB-DDI binder system in a hot stage microscope. When it is gradually heated to about 500 °C, it caused reduction in fluidity and coagulation of binder melt to wet clumps with surrounding fluid. In propellants with a large AP particle size distribution refined particles of titanium dioxide act to enhance the binder melt layer viscosity such that no intrusion with the fine AP particles occurs and natural burning is reinstate. Titanium dioxide is used to equalize pressure exponents and is noted to not play a role of burn rate catalyst.

Carvalheiro15 discovered the thermal decomposition nature of AN/HTPB/Fe2O3 composite propellants and noted that the exothermic peak of the DTA curve is drastically changed by the addition of Fe2O3. This additive causes an increment in the magnitude of the exothermic DTA peaks and a fall in the magnitude of the endothermic DTA peaks.

Singh16 noted that energetic metal salts and complexes should be used as ballistic modifiers for AP-based CSPs. Among all the other additives screened, Transition metal [Mn(II), Fe(II), Fe(III), Co.(II), Ni(II), Cu(II) and Zn(II)] salts of 5-nitro-2,4-dihydro-3H-1,2,4-triaole-3-one (NTO) were concluded to be the best for application in CSPs. Transition metal salts of NTO are in-depth energetic compounds, which putrefy exothermally to give their corresponding transition metal oxides (TMOs). When these salts are introduced in CSPs, the respective TMOs are formed in situ while combustion; these TMOs have a better catalytic activity on the combustion of HTPB-AN CSPs. Some of them were found to enhance the heat released in the condensed phase during slow thermolyzes of the modified propellants. Few important aspects that explains the mechanism of catalyst action are;

1. Metal components in TMO can exhibit variable valence or oxidation states and hence TMO's are effective decomposition and burn rate catalysts.
2. Additives which are electron donors or acceptors can modify oxidation/decomposition products
3. Catalytic activity results from physical contact; the reaction ceases when particles no longer have an oxidizer-additive interface.
4. Gaseous product distribution may be altered by some catalytic agents.
5. Iron compounds are common catalysts for AP propellant systems; a redox-cycle involving the ferric-ferrous couple may be the key mechanism in combustion catalysis by iron compounds.
6. Burn rate depends on catalyst concentration, surface area and state of aggregation.

1.3 Effect of Pressure on Burn Rate
The liner burning rate of the solid propellant enhances with the pressure in which it burns. Rastogi 28 found the following burning rate pressure relationship assuming Tubular Reactor model for composite solid propellant combustion:

\[(r/p)^2 = a/p - b\]

Now it is clearly visible that, although there is a very simple relationship between pressure and burning rate which justify the burning rate of all propellant over a huge range of pressure. However, it is recommended that,

1. At high pressure (above few 100 to 2000 psia, depending composition) the burning rate is an effortless function of the pressure and can be represented adequately by equation (1) or more precisely by equation (2).
2. At intermediate pressure, the pressure dependence may be complex and strongly dependent on composition regions of zero or even negative pressure dependence are sometimes found.

3. At very low pressures, the burning rates of the propellants extrapolate to a finite rate at zero pressure. Although the propellant ceases to burn at pressures somewhere between a few psia to 100psi.

2. Experimental Methodology
The experimental work carried out in the present investigation includes preparation of phase-stabilized Ammonium Nitrate, formulation of propellant composition, preparation of propellant samples and evaluation of combustion parameters of propellant samples with and without catalysts. Thermal analysis was done with the help of Thermo Gravimetric Analyzer (TGA) and Differential scanning calorimetry (DSC). The burn rate studies were done with the help of Crawford Strand Burner.

The experimental work carried out under the scope of present work was divided into two major sections:

| Table 1. Formulation of Composition of Propellants |
|---|---|---|---|---|---|---|
| PSAN | HTPB | DOA | TDI | GLYCEROL | Mno2 | TiO2 | AlO3 |
| 75  | 18  | 5.4 | 1.4 | 0.20  | -   | -   | -   |
| 75  | 18  | 5.4 | 1.4 | 0.20  | -   | 1   | -   |
| 75  | 18  | 5.4 | 1.4 | 0.20  | 2   | -   | -   |
| 75  | 18  | 5.4 | 1.4 | 0.20  | -   | 2   | -   |
| 75  | 18  | 5.4 | 1.4 | 0.20  | -   | -   | 1   |

2.1 Mixing of Ingredients
All the ingredients used for above compositions were stored in a controlled humidity condition. The processing variables like mixing time, mixer temperature and the sequence of ingredient addition into the mixer were kept same in all the mixing. The required quantity of HTPB and DOA were taken in separate stainless steel vessels. HTPB and DOA were dehumidified. Both the liquids were cooled for about 5 minutes. DOA was added into the HTPB vessel and mixed for about 10 minutes. Later, the required quantity of TDI and glycerol were added into the HTPB-DOA mixture and was stirred continuously till the mixture becomes uniform. Then, AN were added into the mixture in three batches. In this experimental work, one part of fine and three parts of coarse particles of Ammonium Nitrate were used into the mixture. Loading AN for upto 75% into the HTPB mixture was very hard. So, the mixing process was conducted in a heated environment for about 60°C and the mixture was continuously stirred, till the mixture became uniform (half an hour was required).

2.2 Curing
The propellant slurry was casted into a rectangular aluminum mould. Before casting, the mould was greased and covered with aluminum foil. The slurry was poured into the mould and was patted to
make it spread uniformly over the surface with the help of a spatula. The casted mould was kept in the oven and the temperature was set depending upon the type of fuel binder used in the propellant composition. For HTPB type of fuel binder, the curing temperature was 60°C for 6 days to have complete cure of the slurry. The plate was then removed from the oven and was allowed to come to the room temperature.

2.3 Preparation of Propellant Strands

The propellant block was cut into rectangular strands of size ‘6mm * 6mm * 80 mm’. These stands were then inhibited from sides by quick-drying polyethene enamel. A uniform coating of paint was ensured and was kept for drying. The propellant samples were kept in polythene bag and stored in a desiccator to avoid moisture absorption.

2.4 Combustion parameter study

To study the combustion parameters of the propellants, work has been carried out in the following direction.

a) Burning rate measurement at various pressures using Crawford Bomb.

b) Thermal decomposition study of propellant using simultaneous thermal analyser.

2.5 Crawford Strand Burner

The burning rate studies of propellant sample were carried out using Crawford high pressure strand burner setup. The study was carried out from 200 psi to 1000 psi at five different pressure ratios. Nitrogen gas was used to pressurize the bomb. The propellant strands of size of length 80 mm and cross section 6 mm × 6 mm used in this experiment.

2.6 Simultaneous Thermal Analyzer

The thermal decomposition studies of HTPB fuel binder and the propellant, with and without catalyst were carried out on a NETZSCH Simultaneous Thermal Analyzer (STA 409 PC luxx). Necessary inputs were given to the NETZSCH-TA4-5 software in the computer. The necessary graphs like TG vs. temperature and DSC vs. temperature were generated directly from the software and were analyzed.

3. Result and Conclusion

3.1 Burn Rate Studies

The burn rate studies at various pressures were carried out using a Crawford Strand Burner. The propellant strands were electrically ignited and the time taken to burn for 50 mm length of the strand was recorded. The burn rate was calculated by dividing length by time taken to burn the length. Nitrogen gas was used to pressurize the strand burner to simulate the operating chamber pressure conditions. At each pressure the burning rate measurements were done twice / thrice to ensure the repeatability of data. The results are presented in table 2.

The following observations have been obtained from the results obtained.

a) All of the virgin PSAN – HTPB propellant strands did not burn completely in the pressure range 200 PSI- 1000 PSI. The strands extinguished after burning about 1 cm from the top.

b) Al2O3 catalyzed samples (both of 1% and 2%) have shown increasing of burn rate trend with pressures as shown in fig 1.

c) Comparing the burning rate at different pressures with 1% Al2O3 and 2% Al2O3, it is found to be nearly same, as shown.
d) TiO2 (1%) catalyzed sample did not undergo combustion till 400 PSI, but has shown proper combustion at higher pressures from 600 PSI to 1000 PSI; TiO2 (2%) catalyzed propellant sample has undergone combustion at all the pressures tested, as shown in Fig 2.

e) Similarly, MnO2 (1%) catalyzed sample had not undergo combustion till 400 PSI test pressure, but had exhibited complete combustion at higher pressures from 600 PSI to 1000 PSI; MnO2 (2%) catalyzed sample exhibited proper combustion at all the testing pressures from 200 PSI to 1000 PSI. This can be clearly seen in Fig 3.

f) Among all the compositions, the MnO2 (2%) catalyzed sample had shown the high burn rate results, which can be observed from the graph shown in Fig 4.
Figure 3: variation of burn with pressure for MnO₂ catalyst propellant

![Figure 3](image)

Figure 4 – Comparison of burn rates of all the propellant samples

![Figure 4](image)

Table 2: Results of the PSAN-HPB propellant Burn rate

| Name Of The Propellant | Burn Rate At 200 Psi(Mm/S) | Burn Rate At 400 Psi(Mm/S) | Burn Rate At 600 Psi(Mm/S) | Burn Rate At 800 Psi(Mm/S) | Burn Rate At 1000 Psi(Mm/S) |
|------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| PSAN(75%)-HTPB         | Did Not Sustain             | Did Not Sustain             | Did Not Sustain             | Did Not Sustain             | Did Not Sustain             |
| PSAN-HTPB              | 0.52503                     | 0.8526                      | 1.0622                      | 1.2893                      | 1.53092                     |
### 3.2 Thermal Decomposition Studies

The thermal decomposition studies of Ammonium Nitrate (AN), Phase Stabilized Ammonium Nitrate (PSAN), virgin PSAN-HPB propellant and catalyzed by metal oxide PSAN-HPB propellant have been separately carried out with Simultaneous Thermal Analysis (STA) NETZCH. The heating rate in all the experiments was kept at 10 °C/min.

### 4 Conclusion

The following conclusions are drawn from the present investigations on the combustion characteristics of PSAN-HPB composite solid propellant with and without catalysts:

1. The PSAN (75%)-HPB composite propellant did not burn at any pressure range. Similarly, PSAN (80%)-HPB propellant. The strand extinguished after burning about 1cm from the top of the strand.
2. The propellant strand with catalyst although ignite at ambient pressure. But could not sustain the burning. The propellant strand extinguished afterburning about 1 to 2 cm from top.
3. Propellant with 1% & 2% Al2O3 catalyst burned at all of the pressures in the range between 200 Psi to 1000 Psi. The burn rates differed marginally when 2% Al2O3 was added in comparison to 1% Al2O3added propellant. Propellant with TiO2 (1%) & MnO2 (1%) catalyst did not burn up to 400 Psi pressure. However after this pressure they burn smoothly.
4. Among all the propellant, the MnO2 (2%) catalyzed sample shows the highest burn rate at all the pressure.
5. All the catalyzed propellant samples had nearly the same endothermic peaks in the same temperature range but the exothermic peak differs in size and position with respect to temperature. The propellant catalyzed by MnO2 has the highest exothermic peak point.
6. Among all the virgin propellants, the 75% PSAN (made by solid mixing)-HPB propellant sample has the highest exothermic peak.

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