

# The pressure effect study on the burning rate of ammonium nitrate-HTPB-based propellant with the influence catalysts

M. Pandey · S. Jha · R. Kumar · S. Mishra ·  
R. R. Jha

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**Abstract** The burning rate of AN–HTPB-based propellant catalysed with chromium salt has been studied using conventional strand burner under the various pressure range, i.e. from atmospheric pressure to 6.897 MPa and verified with Piobert law, i.e.  $r = aP^n$ . At atmospheric pressure, the burning rate AN–HTPB propellant was being accelerated with the chromium-based catalysts used. In case of lead chromate-catalysed system, burning rate was observed 2.655 times higher than burning rate ( $r = 0.200 \text{ mm s}^{-1}$ ) of virgin AN–HTPB propellant sample. However, the Copper chromate-catalysed propellant burned with slower rate ( $r = 0.160 \text{ mm s}^{-1}$ ) than the virgin AN–HTPB propellant sample. The burning rate of all catalysed propellant samples are found to be the pressure sensitive and accelerated higher with rise of pressure. The highest burning rate ( $r = 2.422 \text{ mm s}^{-1}$ ) was recorded with ammonium dichromate and lowest ( $r = 1.40 \text{ mm s}^{-1}$ ) with lead chromate-catalysed propellant sample with the rise of pressure up to 6.897 MPa at different pressures. A linear relationship was observed between the burning rate and pressure rise which followed the Piobert law, i.e.  $r = aP^n$ . The pressure index ( $n$ ) values of AN–HTPB-based samples were calculated higher when catalysed with ammonium dichromate, Copper Chromate,  $\text{Cr}_2\text{O}_3$ , Potassium dichromate ( $n = 0.525, 0.555, 0.429, \text{ and } 0.408$  respectively) and lower ( $n = 0.226$ ) with lead chromate compared to virgin sample ( $n = 0.405$ ). Higher value

indicates the positive effect on accelerating the burning rate with catalyst at higher pressure ranges.

**Keywords** Burning rate · Catalytic effect · Pressure effect · AN–HTPB propellant · Pressure index

## Introduction

The combustion studies on Ammonium Nitrate (AN)-based systems available in literature are far less in comparison to the voluminous account published on AP containing propellants. Several workers have formulated AN-based propellant using different types of binders for the development of reduced smoke propellant. In such studies these propellants have shown their poor performance. With development of energetic binder, the interest in the development of energetic, eco-friendly propellants has revived the efforts in this direction and AN is being considered as the main entity oxidizer for producing clean burning propellants. The enormous challenges in the development of propellant systems with acceptable burn rates, ignition characteristics, ability to combust metals and devoid of volume expansion problem are being taken up with a holistic approach.

Hamilton [1] has formulated a solid propellant with phase stabilized ammonium nitrate with  $\text{KNO}_3$  and fibrous cellulose for inflation of vehicle air-bags, which has relatively low burning rate exponent of  $\leq 0.7$  and has decomposition  $\geq 85\%$  of theoretical decomposition. Batchelder [2] has formulated a smokeless, slow burning and low flame temperature AN and polystyrene propellants using ammonium dichromate as burn rate accelerator. Jones [3] has casted a propellant with granular AN and methylacrylate co-polymer as an elastic, combustible, cross linked

M. Pandey (✉) · S. Jha  
Sikkim Manipal Institute of Technology, Majitar, Sikkim, India  
e-mail: mrpandey1@rediffmail.com

R. Kumar · S. Mishra · R. R. Jha  
Department of Chemistry, Ranchi University, Ranchi,  
Jharkhand, India

resinous fuel. For burn rate acceleration, catalysts were selected from the group consisting of zirconium hydride, cobalt, nickel, alloy of cobalt, nickel and zirconium and oxide of cobalt and nickel. In recent stages, several other binders have been used such as HTPB, CTPB, azide-based energetic binders. These have been found to improve the performance of AN-based propellant. Simoes et al. [4] have used DNAM [4,6-dinitroamino-1,3,5-triazine-2(1H)-one] as an ingredient in PSAN/HTPB-based propellant for performance analysis. Arakawa and Kohga [5, 6] have also studied the effects of surfactants like sodium stearate, sodium linoleate, lauryl amine, and sodium myristate on viscosity and burning rate of uncured HTPB–AN system. Kuwahara and Matsuo [7], whilst studying the burn rate and ignition behaviour of AN/AP containing propellants reported that combustion rate decreases and ignition delay time increases with increasing concentration of AN but the temperature sensitivity remains nearly constant (0.2–0.3%/K). The pressure exponent was found to decrease with increasing AP content in oxidizer. In another study [8], burning rates were found to improve when small amount of AP was added to GAP/AN propellant with diffusion flame of AP becoming the rate determining step at 4 MPa pressure.

Hagihara [9] investigated the effects of organo-metallic compounds of chromium- and cobalt-like chromium acetyl acetonate, cobalt oxide, cobalt stearate and cobalt 2-ethyl hexanoate on burning rate of HTPB–AN composite propellant. The propellants were prepared using the phase stabilized AN for studying the ignition, burning rate with pressure and to understand the processing and stability [10]. It was reported that 3 wt% Ni PSAN/HTPB propellant gives a higher burning rate in comparison to Cu PSAN at similar operating pressures. Brewster et al. [11] used thermocouples and fiber optics to investigate the mechanism of heat transfer and combustion in Mg–AN composite propellants. It was found that a liquid layer at  $300 \pm 30$  °C covers the surface of both the AN and binder regions during combustion. The Mg was noted to burn near the propellant surface in a dual vapour and surface mode producing both fine smoke and large-scale MgO ash. Moreover, burning rate was found to increase significantly with increasing Mg loading due to convective and radiative heat feed back from burning Mg particles that were retained near the propellant surface by large-scale ash and due to condensed phase heat release from magnesium oxidation. Murata et al. [12] have used magnalium (Mg–Al alloy) as a fuel to analyze the combustion characteristic of AN-based solid propellant. It transforms the decomposition characteristic of AN into two-step process and lowered the decomposition temperature, which ultimately enhances the burning rate. Burning rate of AN-based propellants is reported to increase with content of magnalium.

The combustion mechanism of the composite solid propellants is quite complex. A number of models have been proposed to explain the combustion mechanism by different research workers [13–15]. Chaiken and Andersen [16–18] proposed the “thermal layer theory” which is based on the two-temperature postulate and is applicable to ammonium nitrate propellants. It assumes that the solid-phase decomposition is a result of the heat transfer from the flame zone or thermal layer surrounding the oxidizer particles and that this flame zone is a result of the gas-phase redox reactions between the oxidizer and fuel pyrolysis products. This theory states that for AN-based propellants the oxidizer binder gas reactions occur too far from the burning surface to influence to any great extent the heat transfer to the surface.

Carvalho and Campos [19] proposed combustion model AN–HTPB propellant with the concept of multiple competitive flames and separate surface temperatures. It accounts for the phenomenon associated with radiative heat transfer from the various flames and combustion products to the surface of oxidizer particles and fuel binder. Kondricov et al. [20] have worked in the area of combustion for improving the general understanding about pure AN combustion, to clarify the burning properties of broad range of AN-based formulations, and to elucidate some instability affect of pure AN as well as AN-based propellant burning. Their results show that heat release occurs due to condense phase reaction up to 100 atm pressure where as at higher pressure gas-phase flame plays an important role in controlling the burning rate.

The parameter of burning rate is of prime importance since it decides the ultimate use of that particular propellant system. The various performance parameters are related to burning rates like thrust, specific impulse and characteristic velocity [21]. Therefore, it is imperative to detail the knowledge of burning rate of propellant under a wide range of operating conditions to exploits application area more meaningfully. The burning rate depends upon the various factors [22, 23] like pressure, temperature, oxidizer-fuel ratio, oxidizer particle size, etc. the dependency of burning rate of a solid propellant on various factors is expressed by relation

$$R = f(\rho_c, T_i, T_f, U_g, O/F, C-F, O-P, G)$$

In addition to these factors, there are special ballistic effects that cause departures from the standard burning rate laws, other parameters that affect the burning rate are additives, acoustic and specific surface conditions. Seeing the importance of catalytic and pressure effect on the combustion process, the burning rate ( $r$ ) of AN–HTPB-based solid propellants has been studied under various pressure by incorporating 3% catalysts. The burning rate measurements have been done using the conventional

**Table 1** Burning rate of HTPB-AN composite propellants with/without catalysts at 0.092 Mpa pressure and the burn rate ratio of catalysed with virgin propellant

Propellant	Burning rate/mm s <sup>-1</sup>	Ratio	% Rise
HTPB-AN	0.200	–	
HTPB-AN-ADC	0.251	1.255	125.5
HTPB-AN-KDC	0.345	1.725	172.5
HTPB-AN-PbC	0.531	2.655	265.5
HTPB-AN-CuC	0.160	0.8	-80
HTPB-AN-Cr <sub>2</sub> O <sub>3</sub>	0.301	1.505	50.5

strand burner and are verified with Piobert's law (i.e.  $r = aP^n$ ). The result of this study has been used to understand the effect of various catalysts on gas-phase reaction at various pressure ranges.

### Experimental work

The propellant ingredients Hydroxy Terminated Polybutadiene (HTPB)—21.58% as polymeric fuel binder, dioctyl adipate (DOA)—6.48% as plasticizer, toluene 2,4-diisocyanate (TDI)—1.68% as curing agent, Glycerol—0.26% as cross linking agent and AN—70 wt% as oxidiser were weighed and kept under controlled humidity conditions (RH ≈ 45%). The burn rate modifiers like ammonium dichromate (ADC), potassium dichromate (KDC), lead chromate (PbC), copper chromate (CuC) and chromium trioxide (Cr<sub>2</sub>O<sub>3</sub>) of good quality were used in preparing the catalysed propellant compositions. All additives were incorporated at a fixed concentration level of 3 g per 100 g of propellant mix. The prepared propellant blocks were sliced and then cut into rectangular strands of 7 × 7 × 100 mm size.

The burning rates of virgin and catalysed HTPB-AN propellants were studied under different pressures up to 6.897 MPa pressure level using a conventional strand burner [24, 25]. Nitrogen gas (IOLR-3) was used to

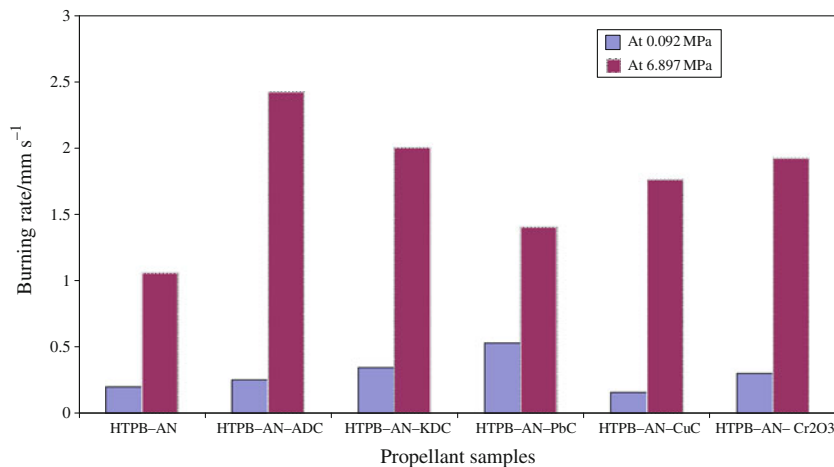
pressurize the bomb. The dial type pressure gauges were used to record incoming pressurant pressure and pressures in bomb and line. A surge tank was provided in the set-up to ensure that a strict pressure level is maintained in the bomb.

### Results and discussion

#### Under atmospheric pressure

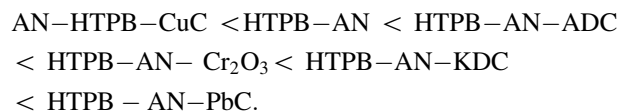
The burning rate for virgin and catalysed propellant strands has been measured under atmospheric pressure and summarized in Table 1. The burning rate of AN-HTPB virgin propellant was found to be 0.2 mm s<sup>-1</sup> (±0.005) and which was accelerated by catalysts. Burning rate of AN-HTPB-based propellants was raised by 1.255 times in case of ADC-catalysed system to 2.655 times in case of PbC-catalysed system. However, burning rate of CuC-catalysed AN-HTPB propellant was only 0.160 mm s<sup>-1</sup> which was lower than the burning rate of virgin one. This variation can also understand through bar chart (Fig. 1). The higher and lower burning rate can be explained with the decomposition behaviour. As it was reported that AN decomposed endothermically with and without CuC but exothermically with ADC, KDC, PbC and Cr<sub>2</sub>O<sub>3</sub> catalyst [26] at atmospheric pressure. Further, Chaiken and Andersen's theory [16–18] states that for AN-based propellants, at atmospheric pressure, the oxidizer binder gas reactions occur too far from the burning surface to influence to any great extent the heat transfer to the surface. Thus, for the continuous combustion of AN-based propellant and its acceleration with catalyst in the burning, combustion has to depend more upon thermal decomposition heat energy at the sub surface.

The higher burning rate of AN-HTPB with the catalysts like ADC, KDC, PbC and Cr<sub>2</sub>O<sub>3</sub> is because of alternation

**Fig. 1** Bar chart of the burning rate of virgin and catalysed AN-HTPB based at 0.092 and 6.897 MPa pressure

of decomposition reaction from endothermic to exothermic and heat generated during subsurface decomposition reaction. It is worth mentioning that carbonaceous ash skeleton was also found after the burning of strands in both the cases, suggesting that binder combustion remains incomplete at atmospheric pressure as well as insufficient heat feed back from gas-phase reaction (i.e. from flame zone) to the subsurface.

On the basis of their burning rate, the propellants can be arranged as:



The results show that catalysts alter the burning rate by influencing the oxidizer, binder pyrolysis rate and also possibly the binder-oxidizer interfacial interaction.

#### Under pressure effect

All the propellant samples were also burned under the various pressures, i.e. at 1.379, 2.759, 4.138, 5.517 and 6.897 MPa, of inert atmosphere of N<sub>2</sub> gas, to understand effect of pressure along with catalysts. In the various models [13–19], pressure was represented as responsible factor for reducing the flame distance from the surface and enhancing of more heat feedback that alternatively increases the burn rate by accelerating the surface decomposition. The mean burn rate with corresponding pressure for each propellant samples measured has been summarized in Table 2. The graphs (Figs. 2, 3) between the pressure (ln *p*) verses burning rate (ln *r*) were plotted, which give nearly a straight line. Their pressure index '*n*' and constant '*a*' were calculated with the help of measuring the slope and intercept. The verification of results with the help of Piobert law (i.e.  $r = aP^n$ ) indicates that burning rate in all cases are pressure sensitive and showing a linear relationship with rise of pressure.

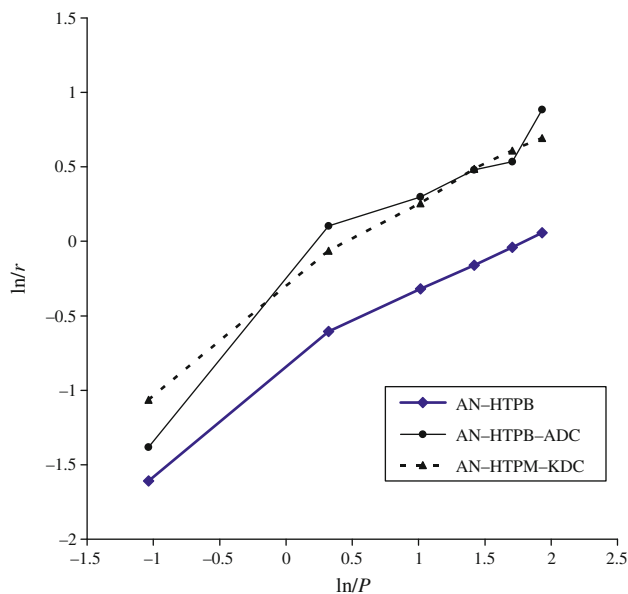
The burning rate of AN-HTPB virgin sample was found to accelerate with the rise of pressure (Table 2). The burning rate of virgin sample rose by 5-fold with the rise of pressure from 0.092 to 6.897 MPa, and its pressure index (*n*) was calculated ( $n = 0.405$ ). The increased burn rate with pressure can be explained with the help of various combustion models. Rising of the pressure suppresses the flame distance from the surface and which ultimately increases the heat feedback from gas phase to surface. The increased heat feedback enhances the binder-oxidizer decomposition reaction in the subsurface and the rate of gasification. The rate of gasification and the mixing of decomposition products in gas phase finally control the gas-phase reaction. The suppression of gas phase distance

**Table 2** Effect of pressure on burning rate of virgin and catalysed HTPB-AN composite propellants

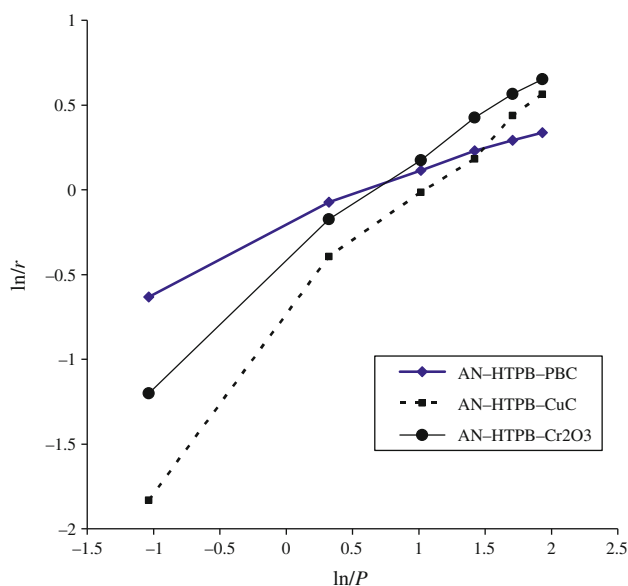
System	Pressure/ MPa	Burn rate/ mm s <sup>-1</sup>	<i>n</i>	<i>a</i>
HTPB-AN	0.092	0.200	0.405	0.480
	1.379	0.546		
	2.759	0.724		
	4.138	0.852		
	5.517	0.960		
	6.897	1.059		
HTPB-AN-ADC	0.092	0.251	0.525	0.878
	1.379	1.108		
	2.759	1.348		
	4.138	1.617		
	5.517	1.708		
	6.897	2.422		
HTPB-AN-KDC	0.092	0.345	0.408	0.912
	1.379	0.939		
	2.759	1.29		
	4.138	1.628		
	5.517	1.840		
	6.897	2.000		
HTPB-AN-PbC	0.092	0.531	0.226	0.910
	1.379	0.93		
	2.759	1.12		
	4.138	1.26		
	5.517	1.340		
	6.897	1.40		
HTPB-AN-CC	0.092	0.160	0.555	0.602
	1.379	0.674		
	2.759	0.984		
	4.138	1.20		
	5.517	1.55		
	6.897	1.757		
HTPB-AN-Cr <sub>2</sub> O <sub>3</sub>	0.092	0.301	0.429	0.839
	1.379	0.84		
	2.759	1.19		
	4.138	1.53		
	5.517	1.76		
	6.897	1.92		

from surface with increased heat feedback ultimately enhances the decomposition process of oxidizer and binder at subsurface and the rate of gasification which yields burn rate of the propellant samples. Even at higher pressure, complete combustion was observed as no ash was observed.

All the catalysts accelerate the burn rate propellant sample along with the rise of pressure. At higher pressure (i.e. at 1.379, 2.759, 4.138, 5.517 and 6.897 MPa), the increased burn rates were observed with catalysed samples



**Fig. 2** Effect of pressure on burning rate of virgin and catalysed AN-HTPB propellant



**Fig. 3** Effect of pressure on burning rate of catalysed AN-HTPB propellant samples

compared to virgin AN-HTPB sample. The measured burning rate ( $r = 2.422 \text{ mm s}^{-1}$ ) and pressure index ( $n = 0.552$ ) of ADC-catalysed AN-HTPB sample was highest amongst all the systems at 6.897 MPa pressure. The Table 2 shows that the burning rate of ADC-catalysed system is even more than twice that of the virgin sample at the same pressure. Surprisingly, the burning rate of PbC-catalysed system was recorded as more than twice that of the virgin's and ADC-catalysed system and higher than

that of KDC-catalysed system at atmospheric pressure. However, with the rise of pressure, the burning rate of PbC-catalysed system did not rise so much, and its pressure index was observed even lower than that of the virgin one. The burning rate of PbC-catalysed system was lowest amongst the all catalysed systems when pressure was maintained at 6.897 MPa.

At atmospheric pressure, the burning rate of KDC-catalysed propellant was measured more than ADC-catalysed system and less than PbC-catalysed system. With increase in pressure, with KDC system burning rate was accelerated faster than PbC-catalysed system and slower than ADC-catalysed propellant. As a result, at the pressure of 6.897 MPa, the burning rate value was obtained lower than the rate of ADC-catalysed system and higher than the rate of PbC system and its pressure index was slightly higher ( $n = 0.408$ ) than that of the virgin sample. With the increase in pressure, the burning rate of CuC-catalysed system was enhanced dramatically to yield the highest pressure index value ( $n = 0.555$ ). It even reduced the burning rate to  $0.160 \text{ mm s}^{-1}$  at atmospheric pressure which was less than burn rate of virgin AN-HTPB sample, i.e.  $0.200 \text{ mm s}^{-1}$ . The burning rate of CuC raised ten times more with rise of pressure from 0.092 to 6.897 MPa, but still at 6.897 MPa pressure its burning rate was slower than of ADC, KDC and  $\text{Cr}_2\text{O}_3$ -catalysed system. The burning rate of  $\text{Cr}_2\text{O}_3$ -catalysed system was higher than CuC and ADC-catalysed system and lower than that of the KDC and PbC-catalysed system at atmospheric pressure. Its burn rate was accelerated with the rise of pressure in such a way that its burn rate is observed higher than PbC and CuC-catalysed systems and lower than that of ADC and KDC-catalysed systems at the pressure of 6.897 MPa.

## Conclusions

The study indicates that pressure and catalyst both accelerate the burn rate by affecting the decomposition at surface and the combustion reaction mechanism in gas phase. As it is reported in literature [13], rise of pressure decreases the distance of flame zone and increases the heat feed back from flame zone to subsurface zone which accelerates the decomposition process of AN-HTPB and rate of gasification. However, CuC shows reduced value of burning rate in comparison to virgin system at atmospheric pressure and at higher pressures burn rate increases. It possibly promotes gas-phase reaction by its presence in the interface between the solid oxidizer and solid fuel. ADC nearly doubles the burn rate in comparison to virgin propellant and is expected to show greater influence at still higher pressures.  $\text{Cr}_2\text{O}_3$ , KDC greatly influence the gas-phase combustion, consequently delivering the best burn rate excepting ADC. The

effective catalysts marginally increase the combustion index ' $n$ ' in comparison to virgin whereas PbC decreases it

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