Solid Fuel-rich Propellant Development for use in a Ramjet to Propel an Artillery Shell

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ABSTRACT

This study describes the development of a fuel-rich propellant to be used in a solid fuel ramjet to provide active propulsion to a 155 mm artillery shell. Fuel-rich propellants consisting of aluminum, ammonium perchlorate and hydroxyl terminated polybutadiene were developed and their ballistic properties were measured to choose the appropriate fuel for the ramjet application. The attempts made were to enhance the burn rates of the propellant to provide required burn rates at lowest possible pressures in primary combustor of the ramjet. The propellant selection was done with reference of working time period of the base bleed unit, to calculate the required burn rate and corresponding pressure in primary combustor. It was observed that the fuel rich propellant of composition 35% ammonium perchlorate with 1 % Iron oxide embedded on it, 30 % mechanically activated aluminum with 10% polytetrafluoroethylene, and 25 % HTPB was found suitable for the above application. This provided the higher burn rates among all developed propellants with high pressure index of 0.58. This makes it suitable for the ramjet requiring higher burn rates at lower possible primary chamber pressures. The Young's modulus and tensile strength of this propellant was measured to be 1.73 MPa and 0.24 MPa, respectively.

Keywords: 155 mm shell; Artillery shell; Ramjet; Fuel-rich propellant; Range enhancement

NOMENCLATURE

A/F	Air to fuel ratio
Al	Aluminum
AP	Ammonium perchlorate
B	Boron
DAQ	Data acquisition system
DOA	Di octyl adipate
E_S	Secant young's modulus
GAP	Glycidyl azide polymer
HTPB	Hydroxyl-terminated polybutadiene
IPDI	Isophorone diisocyanate
I_{SP}	Specific impulse, m/s
L_f	Length of the propellant grain, m
Mg	Magnesium
P_{C1}	Primary chamber pressure, N/m²
P_{C2}	Secondary chamber pressure, N/m²
PTFE	Polytetrafluoroethylene
SFRJ	Solid fuel ramjet
a	Burn rate of propellant at 1 bar, mm/s
n	Pressure index
$\dot{r}$	Burn rate, mm/s
t_b	Propellant burn out time, s
ρ_p	Density of propellant, kg/m³

1. INTRODUCTION

Artillery guns have played an important role in the wars of the past and remain an essential part of any modern army. The range of the projectile delivered from an artillery gun is an important parameter. The most commonly used 155mm artillery gun has a typical range of 24 km without range enhancement devices.

To further improve the range of an artillery shell, two methods, namely base bleed and rocket assisted projectile have been incorporated till date[1-4]. In the base bleed method, the shell is attached with a gas generator at its rear end which houses a slow burning propellant in it. During the flight, the propellant burns to produce gases which are then injected into the low-pressure region created at the rear end of the shell. This mainly reduces the wake drag acting on the shell and hence, increases the range[1-3]. However, this does not produce any significant thrust and therefore the enhancement in the range is limited to 5% to 30% as indicated by Gany[1] and Zhang & Zheng[2]. Another way to improve the range is to provide thrust during the flight by using a solid rocket to counter the drag. However, a solid propellant has lower specific impulse (I_{SP}), defined as thrust per unit mass flow rate of propellants of around 2400Ns/kg. Also, the volume available on the shell places a limit on the maximum mass of propellant that can be accommodated in the shell. The above mentioned constraints, limits the overall impulse provided by the rocket engine.

Another promising way to increase the range of shell is to use a solid fuel ramjet (SFRJ) to provide active propulsion during the flight. Being an air-breathing engine, ramjet has higher I_{SP} (> 4000 Ns/kg) compared to a solid rocket. A solid rocket carries both fuel and oxidiser as compared a ramjet, which carries only fuel and obtains oxidiser from the

surrounding atmosphere and therefore provides the higher overall impulse to shell for the same mass of propellant. The muzzle velocity[5] of an artillery shell is around Mach 2. This fact makes the use of ramjet attractive as its operating range Mach number is between 2 to 3. The Norwegian International Aerospace and Defence Company 'NAMMO' has initiated a similar technological program on the range enhancement of an 155 mm artillery shell using a solid fuel ramjet. As per their claim the shell could achieve the range more than 100 km using a 52-calibre gun, which is a significant improvement on the existing range. However, more details on the propellant type and other details are not readily available.

Missile systems like *Akash* of India, Meteor of France, GQM-163 Coyote of United States of America make use of solid fuel ramjet (SFRJ) for their propulsion. Various researchers[6-8,11]) have proposed the use of fuel-rich propellant for ramjets in their work. Figure 1 shows the schematic of the solid fuel ramjet in fuel-rich configuration with two combustors. In the primary combustor, the fuel-rich propellant is used in an end burning configuration. A fuel-rich propellant has a small amount of oxidizer added in it, which allows self-sustained combustion of the fuel-rich propellant. The burn rate of the propellant depends on the pressure inside the primary combustion chamber, P_{C1}. The burning of the fuel-rich propellant produces high-temperature fuel-rich gases. These gases are ejected through a primary nozzle into the secondary combustor. Due to flow being chocked through the primary nozzle, P_{C1} remains constant with time, irrespective of the pressure in the secondary combustor, P_{C2}. The products of combustion of the fuel-rich propellant undergo further oxidation with the compressed air rammed-in through the air intake. This produces high-temperature gases which expand through the secondary nozzle, to provide thrust.

The propellant and its properties have to be known to obtain the corresponding trajectories of the shell with the ramjet. It is required to develop a suitable fuel-rich propellant for the current application. Use of metalised fuels has been suggested by many researchers[6-13] due to the high heat of combustion of metals. Higher heat of combustion results in a higher combustion temperature and hence higher exhaust velocity which leads to larger thrust. Metals have high volumetric and gravimetric heat release compared to polymeric fuels[10-16,21]. Higher volumetric heat release, with the use of metals in the propellants could result in a higher density of the propellant and hence a compact propulsion system. In the current application, compactness of the propulsion system is a crucial element. Aluminum (Al), Boron (B) and Magnesium (Mg) are the most commonly used metal fuels.
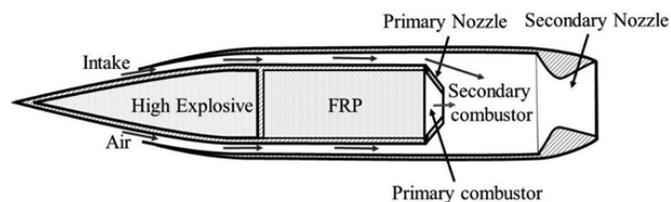

Figure 1. Schematic of artillery shell with ramjet in fuel-rich mode.

One of the most challenging aspects of the fuel rich propellant is that if the AP content is not high enough it will lead to larger residue while if it is high it leads to lower specific impulse. Efforts were made to develop a propellant which provides zero residue and have higher pressure exponent in order to provide higher burn rates at lower possible primary chamber pressures. Here in the current work the overall length of the artillery shell is restricted to 7 times of its diameter so that it can be spin controlled[18]. This in turn restricts the length of the primary combustion chamber to be around ~200 mm. Here, the air intake is assumed to deliver the correct mass flow rate of air and has not been designed.

Temperature sensitivity, σ_T is another important parameter for the fuel development, especially for the current application as shell may be fired from the various places with different temperature conditions. Low temperature sensitivity is must to ensure not much variation in ramjet performance, when fired at different ambient temperature conditions. Also, good mechanical properties of the propellant have to be ensured as it undergoes the high stresses due to a very high accelerations in the barrel when fired. The temperatures sensitivity study and mechanical and physical properties of the propellant developed has also need to be carried out.

2. PROPELLANT DEVELOPMENT

Zongqin[7], *et al.* studied the combustion efficiency of ramjet with Al/AP/HTPB based fuel-rich propellant. The 30% increase in combustion efficiency and reduced two phase flow were observed due to enhanced mixing in secondary chamber. Kubota and Kuwahara[8] studied the combustion of glycidyl azide polymer (GAP) based fuel rich propellant for ducted rockets, which was observed with higher specific impulse (I_{SP}) and burn rates compared to typical AP/HTPB based solid propellant. Shin[14], *et al.* developed the Boron based fuel rich propellant to be used in a ducted rocket to achieve the higher pressure exponent.

A good review of the literature on this topic and advantage of using aluminised fuel-rich propellant has been brought out by Rathi & Ramakrishna[11]. They have argued that a propellant which has lower residue is preferred in any propulsion system. Rathi and Ramakrishna[11] had developed an aluminised AP/HTPB based fuel-rich propellant, which resulted in zero residue. Micron-sized flake like Al (pyral) with very high specific surface area (23 m²/g) was used in the propellant, following the work of Verma & Ramakrishna[17] with regards to composite solid propellant. As reported by Verma & Ramakrishna[17], the thickness of pyral (32 nm) was less than that of the micron-sized spherical Al (5.65 μm - 25 μm) and hence its combustion occurred closer to the propellant surface. This resulted in a higher heat feedback from aluminum combustion occurring closer to the surface of the propellant and thereby increasing the burn rates.

Initially, aluminised AP/HTPB based fuel rich propellants with compositions similar to developed by Nanda & Ramakrishna[9] were developed which had 30 % AP with variety of catalysts to enhance the burn rates. However, all the propellants were observed to have residue of around 20% - 25%. An aluminised propellant was developed with 35 % AP

as reported by Rathi & Ramakrishna[11], which resulted in zero residue. This propellant was used as a baseline propellant due to its higher burn rates and zero residue. Further four more propellants were developed to improve the burn rates further, to identify the best possible candidate to be used in the ramjet assisted artillery shell.

As was observed by Rathi & Ramakrishna[11], the increase in solid loading of fuel-rich propellant not only reduced the residue, it also resulted in higher density and higher burn rates among all the fuel-rich propellants developed. Therefore, the propellant F2 (refer Table 1) was developed by increasing the Al content from 30 % to 45 % by weight, to see the possible enhancement in burn rates. This propellant was made using pyral initially. However, due to increase in viscosity of the propellant, it did not cure even after a period of two months at the elevated temperature of 60 °C. This was possibly due to the large fraction of fine sized Al particles, which prevented the binder from cross linking. Therefore, the pyral was replaced with relatively coarser spherical Al of average particle size 6.5μm to prepare the propellant F2 with increased solid loading.

Aluminum with fluorine containing oxidiser such as PTFE has been suggested by many researchers[19-21] for the better combustion of Al. As reported by Sippel[19], *et al.* and Gaurav & Ramakrishna[20], fluorination of aluminum results in a very high heat release compared to its oxidation. The fluorides of metals are more volatile than the corresponding oxides as reported by Valluri[21], *et al.* Also, according to Valluri[21], *et al.*, adding fluorine as an oxidizer for metal combustion makes it possible to generate more gaseous products and thus reduces the two-phase loses caused by formation of condensed metal oxides. Therefore, if the Al were to be activated with fluorine-based compounds such as polytetrafluoroethylene (PTFE), it could increase the reactivity of aluminum and hence lead to higher burn rates. Following these works, a fuel-rich propellants, where Al was mechanically activated with PTFE were developed in two variants (propellants F3 and F4) as shown in Table 1. Due to the higher binder content in propellant F3 and F4 compared to the propellant F2 and also particle of Al-PTFE (~ 75 μm) being much larger than pyral, there was no problem while curing this propellant. Figure 2 (a) shows the particle size distribution of spherical Al, Pyral and Pyral activated with PTFE, obtained using Malvern Instruments particle analyser (Malvern mastersizer 3000).

Gaurav[22], *et al.* have discussed the effectiveness of embedding iron oxide (IO) on AP. They reported a 30 % increase in burn rate with 1 % IO using this technique as compared to just mechanical mixing. The fundamental reason why embedding catalyst on AP was found to be more effective than mixing was that these catalysts act on AP alone[22,23]. In the case of just mixing these catalysts in the propellant, it gets dispersed and the interaction sites between AP and catalyst are limited. Whereas, in the case of embedding, the catalyst would be in direct contact with AP, and thus more effective. Therefore, propellant F5 was prepared with both activated Al and AP embedded with IO as shown in Table 1.

2.1 Preparation of Propellant

AP and Al were sieved to the required particle size. The particle size distibustion of AP and AP acivated with IO obtained after sieving are as shown in Fig. 2(b). The procedure used for the embedding of IO on AP follows the procedure described by Ishitha & Ramakrishna[23]. All the solid ingredients were kept in an oven at 60 °C for at least 24 h to ensure the removal of any moisture present in it before their use. The binder was prepared in a beaker by adding 77 % HTPB, 15 % Di octyl adipate (DOA) and 8 % Isophorone disocyanate (IPDI). The mix was stirred well for around 5 min. AP and Al powder were then added to the binder in required quantities. A weighing balance with least count of 0.01 g was used to weigh the ingredients. The ingredients were then hand mixed for 5 min to prepare a slurry. The slurry was poured in to a sigma mixer, where it was mixed further for around 45min. The propellant was taken out and poured in to the plastic casing for curing. The casing was kept in a desiccator under an absolute pressure of 50 mm of mercury for 24 h. This ensured the removal of all trapped gasses from the slurry. The slurry then was cured at ambient conditions for 6 to 7 days. The cured propellant was then taken out from the casing and cut into the samples of size 5 mm x 5 mm x 10 mm for burn rate tests.
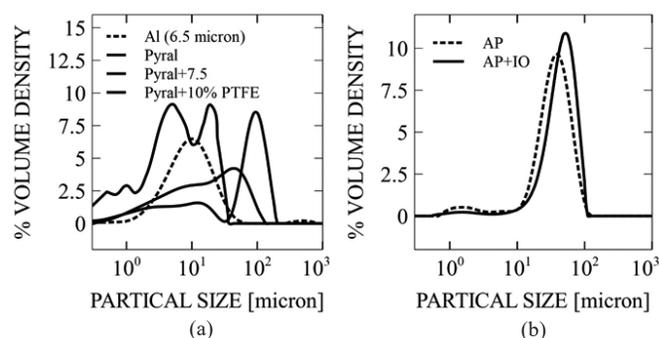

Figure 2. Particle size distribution of (a) spherical Al, Pyral and Pyral activated with 7.5% and 10% PTFE and (b) AP and AP embedded with IO, used to prepare the fuel-rich propellants.

2.2 Experimental Setup and Procedure
2.2.1 Burn Rates and Temperature Sensitivity Measurement

The burn rates of the propellants were measured at various pressures using a standard Crawford bomb as described by Gaurav & Ramakrishna[20]. Figure 3 shows the schematic of the Crawford bomb setup. It consists of a cylindrical high – pressure vessel in which the propellant samples were burnt. The vessel was made of stainless steel and was designed to withstand

Table 1. Composition of fuel-rich propellants

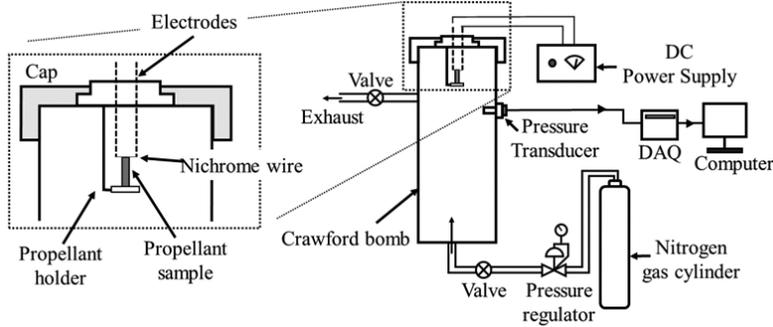| Fuel-rich propellants	AP wt%	IO wt%	Al wt%	PTFE wt%	Binder wt%
F1	35	-	30 (pyral)	-	35
F2	35	-	45 (6.5 μm)	-	20
F3	35	-	30 (pyral)	7.5	27.5
F4	35	-	30 (pyral)	10	25
F5	34.65	0.35	30 (pyral)	10	25

Figure 3. Schematic of the experimental setup to test the burn rates of the propellant.

pressures up to 200 bar. Piezo-electric pressure transducer was mounted on the Crawford bomb to measure the chamber pressure. The bottom of the Crawford bomb was connected to a nitrogen cylinder through a pressure regulator. Nitrogen was chosen to maintain an inert atmosphere in Crawford bomb during the burning of the propellant. An exhaust pipe was connected to the Crawford bomb to expel burnt gases after the test. As seen in the Fig. 3, a propellant holder was provided to place the propellant sample inside the vessel. Electrodes were provided in the holder to make electrical connections with the propellant sample. The vessel was sealed with a threaded cap at the top during the test. The pressure transducer was connected with a computer through a data acquisition system (DAQ) to acquire the pressure data from the Crawford bomb during the test.

The propellant sample was coated with an inhibiter on its lateral faces, along the length prior to the test. This prevents burning of propellant from the sides and allows it to burn uniformly from the top to the bottom. The sample was then placed on the holder after measuring its length carefully with a Vernier calliper of least count 0.02 mm. The electrodes were connected using a Ni-chrome wire. The Ni-chrome wire was kept in contact with the top surface of the propellant sample. As shown in Fig. 3, electrodes were connected to a DC power supply. The top of Crawford bomb was then closed tightly with a threaded cap.

The Crawford bomb was filled with the nitrogen gas from the nitrogen cylinder. The pressure was set to the pre-determined value using a pressure regulator. Once the desired pressure was achieved and was steady, the electric supply was provided to the Ni-chrome wire through the electrodes. The power supply was set to a voltage of 15 V and 10 A current, enough to turn the Ni-chrome wire red hot. This in turn ignites the propellant sample. The exhaust valve was kept slightly open during the test to limit the rise in pressure to 1 bar. The variation in pressure with time was recorded through the DAQ.

The burn time of the propellant was calculated from the pressure-time curve obtained, which is the time between the point of pressure rise after ignition and the point at which the pressure drops indicating the end of burning of the propellant. The burn rate of the propellant was calculated by dividing the measured length of the sample by the burn time. At each initial pressure the test was repeated thrice to ensure repeatability. The results reported in this paper are the average of these three

readings. The maximum dispersion from the mean was 5 %. The tests were repeated at different pressures to obtain the burn rate law of the propellant.

The temperature sensitivity of the propellant was calculated by measuring the burn rates at two different initial temperatures of 30 °C and 70 °C at constant pressure, using the Eqn. (1). The tests were repeated at two different pressures to obtain the variation of temperature sensitivity with pressure.

$$\sigma_T = \frac{2}{\dot{r}_2 + \dot{r}_1} \frac{(\dot{r}_2 - \dot{r}_1)}{(T_2 - T_1)} \qquad (1)$$

2.2.2. Mechanical and Physical Properties Measurement

Uniaxial tensile tests were conducted to measure the mechanical properties of the fuel rich propellant using a computerised universal test machine zwick/roell Z0.5. The samples of propellant were cut in to dimensions as per ASTM D 638 standards as shown in Fig. 4. The average cross-sectional area of the samples measured was 37.8 mm^2. The constant displacement rate of 50 mm/min was applied until the fracture. The data of variation in stress and strain with time, considering the grip to grip distance was extracted.

3. RESULTS

The burn rate tests were conducted for the fuel rich propellants in the Crawford bomb as described in the earlier section. It was observed from the burn rate tests that all the five of the developed fuel rich propellants had zero residue. The measured burn rates of the propellants at different pressures are as shown in Fig. 5. It is apparent that, compared to the propellant F1, propellant F2 which had a higher Al loading,
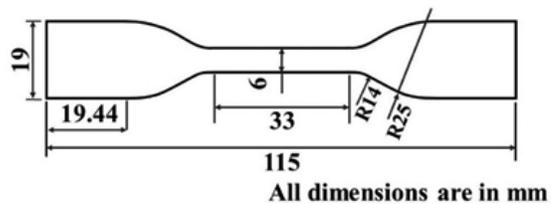

Figure 4. Dimensions of the propellant specimen as per ASTM D 638 standard.
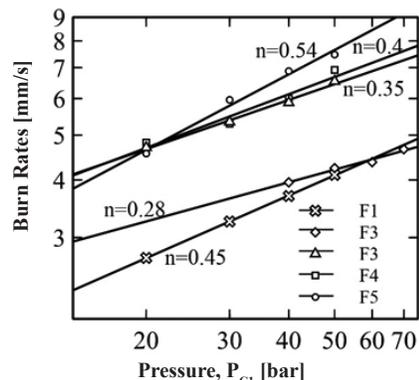

Figure 5. Experimentally measured average burn rates of the fuel-rich propellants at different pressures.

has higher burn rates for pressures up to 60 bar. However, there is a drop in the pressure index, *n* from 0.45 to 0.28 and therefore the burn rates at higher pressures (above 60 bar) are comparatively lower. The reduction in the value of *n* is in agreement with results observed by Verma & Ramakrishna[17], where they reported that the value of *n* increases with a reduction in the particle size of the Al. Unlike propellant F1, where pyral having particles of nano-sized thickness was used propellant F2 was developed with micron-sized Al particles, which resulted in the reduction in pressure index.

As seen in the Fig. 5, due to the use of mechanically activated Al by PTFE, the burn rates obtained for the propellants F3 and F4 were higher compared to both F1 and F2 at all pressures. Around 60 – 75 % higher burn rates were observed due to the use of both PTFE and pyral in the propellants. However, pressure index was observed to be decreased from 0.45 for the propellant F1 to 0.35 and 0.4 for the propellants F3 and F4, respectively. These propellants had same loading of AP and pyral as F1 but with 7.5 - 10 % PTFE (ref Table 1). The decrease in *n* is similar to the results obtained by Gaurav & Ramakrishna[20]. It was argued in their studies that there are two competing factors, one decrease in the value of *n* due to the reduction in thermal conductivity of the propellant on introducing PTFE and another increase in *n* due to the increase in the premixing of Al and PTFE. Between F1 and F3/F4 the former factor was found to be more predominant while between F3 and F4 the latter was more predominant.

It is apperent in the Fig. 5 that the propellant F5 provides highest burn rates among all the propellants with 68 % to 86 % increase in burn rates due to use of both burn rate modifier IO embedded on AP and activated Al with PTFE. Following Ishitha & Ramakrishna[23], the reason for the increase in *n* when AP was embedded with IO was probably due to the reduced binder melt associated with IO addition. The burn rate law obtained for all the fuel-rich propellants and their measured density are tabulated in Table 2.

4. PROPELLANT SELECTION

Propellant for the current application has to have zero residue and high enough burn rates to provide required mass flow rate of the fuel at a reasonable pressure in the primary combustion chamber (P_{C1}). If P_{C1} required is high, the thickness of primary combustion chamber would be large, consequently increasing the weight of the shell and decreasing the propellant loading. All the compositions tested here had zero residue. However, the burn rate requirement of the fuel depends on the thrust requirement, design A/F ratio and, dimensions of the fuel grain. These design parameters have to be optimised to maximize the range of the shell and this is beyond the scope of

the current work. Therefore, an alternate way was proposed to choose the propellant.

The base bleed unit operates around 33 s [24,25] in base bleed assisted shell. Assuming the operational period of ramjet, t_b to be same as that of base bleed operational period, the required burn rate of the propellant for a given length of the propellant grain can be calculated as Eqn. (2).

$$\dot{r} = \frac{L_f}{t_b} \qquad (2)$$

From the required burn rate of propellant, the pressure requirement in the primary combustion chamber can be obtained from the Eqn. (3).

$$\dot{r} = a P_{C1}{}^n \qquad (3)$$

Assuming the grain length, L_f to be 200 mm as explained in the introduction section, the required $\dot{r}$, and corresponding P_{C1} calculated for all the above propellants are as shown in Table 3. It is apparent from the Table 3 that required P_{C1} for the propellants F3, F4 and F5 are all feasible for a burn time of 33 s. However, if the burn time were to be halved, then only F5 looks to be a good alternative, primarily due to the higher *n* associated with it.

The temperature sensitivity of the propellant F5 was measured as explained earlier, at pressures of 40 bar and 60 bar. The results obtained is as shown in Table 4. The obtained value of temperature sensitivity is similar to that of conventional HTPB based solid propellant[26].

The uniaxial tensile tests were conducted for three samples of propellant F5. The obtained stress-strain curve is as shown

Table 3. Primary combustor pressure requirement for grain length, L_f=200 mm and burn time, t_b=33s and 16.5s

Fuel-rich propellants	t_b=33 s		t_b=16.5 s	
	$\dot{r}$ [mm/s]	P_{C1} [bar]	$\dot{r}$ [mm/s]	P_{C1} [bar]
F1		121.1		565.2
F2		188.4		2240
F3	6.061	43.8	12.122	317.1
F4		34.2		193.6
F5		33.5		120.9

Table 4. Temperature sensitivity of propellant F5 at different pressure.

Pressure [bar]	Temperature sensitivity [%/K]
40	0.19
60	0.17

Table 2. Properties of the fuel-rich propellants measured.

Fuel-rich propellants	Average measured density, ρ_p (Theoretical density) kg/m³	Burn rate law
F1	1528 (1531)	$\dot{r}[mm/s] = 0.7 P_{C1}[bar]^{0.45}$
F2	1800 (1806)	$\dot{r}[mm/s] = 1.398 P_{C1}[bar]^{0.28}$
F3	1635 (1640)	$\dot{r}[mm/s] = 1.615 P_{C1}[bar]^{0.35}$
F4	1670 (1680)	$\dot{r}[mm/s] = 1.475 P_{C1}[bar]^{0.40}$
F5	1676 (1684)	$\dot{r}[mm/s] = 0.91 P_{C1}[bar]^{0.54}$

in Fig. 6. Due to the viscoelastic nature of the propellant, it is challenging to obtain the initial Young's modulus for propellant F5. Therefore, the secant of Young's modulus, E_S at 5 % strain was calculated as this has been the accepted norm for these class of materials[27,28]. The average value of E_S obtained is 1.73MPa. The average value of tensile strength measured was 0.24 MPa. The percentage elongation of the propellant was calculated to be 20.5 %.
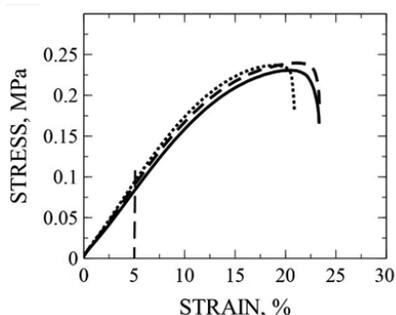

Figure 6. Stress-strain curve obtained for the samples of propellant F5.

5. CONCLUSIONS

A new class of fuel-rich propellants with Al, AP and HTPB were developed to meet the challenging requirements of propelling an artillery shell with ramjet. The challenging task in this work was to design a fuel rich propellant that can withstand the mechanical shock at the time of launch. These propellants were required to have zero residue and also have adequately high burn rates at reasonable pressures. The fuel rich propellant developed here had both aluminium activated with polytetrafluoroethylene and ammonium perchlorate embedded with Iron oxide to enhance their burn rates. The other major challenge that this propellant development overcame was the low burn rate pressure index associated with fuel rich propellants. This would be essential, if a larger thrust were to be required from the system as propellants with higher burn rate pressure index achieve the required burn rates at a lower pressure.

Further, there needs to be directed effort to enhance the mechanical properties of the propellant developed here so as to meet the requirements of the base bleed propellant[29]. As base bleed propellant has the following mechanical properties, Young's modulus 8 MPa, tensile strength 1.1 MPa and percentage elongation 50 %, which make it withstand the shock load on the propellant. Hence, the ramjet fuel developed needs to also have similar mechanical properties. One way to attain the same may be to increase the DOA content which is the plasticizer in the binder.

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