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Combustion Behavior of the Low-Smoke Level Fuel-Rich Composite Propellants at Low Pressure

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Abstract: The combustion behavior of composite fuel-rich propellants based on hydroxy-terminated polybutadiene pre-polymer (HTPB)/ammonium perchlorate oxidizer (AP) studied experimentally at 0.1 − 1 MPa. Results show that high content and small particle size of AP, high pressure promotes sustained combustion and increases burning rate, combustion efficiency and decreases ignition temperature. The copper chromite (CC) as a burning rate accelerator, moderately, increases the burning rate over the whole pressure regime. Moreover, it creates an acceptable combustion efficiency of about 96%. 6% CC decreases ignition temperature by about 16%. It is indicated that the Vieille burning rate law for this propellant family may be extended to extremely low pressures and combustion efficiency marked from "highly poor" to "poor" for the formulations without copper chromite.

Key words: physical chemistry; composite propellants; fuel-rich propellants; burning rate; copper chromite
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1 Introduction

Fuel-rich propellants typically used for ramjet-rocket motors, which also called air-breathing systems. The ramjet-rocket motor consists of two combustion chambers: the fuel-rich propellant is placed in the primary combustor that serves as a gas generator. The combustible, partially burned products generated in this combustor are ejected into a secondary ramjet-combustor and continue to burn with the incoming atmospheric air[1]. Being an air-breathing engine, the energetic performance of the ram rocket is much higher than that of conventional rockets according to the specific propellant formulation, flight Mach number and the inlet pressure of the secondary chamber (0.6 MPa maximum) which, for design optimization, require low-pressure combustion regimes at the first chamber[2]. The specific impulse produced from an air-breathing engine can be double or triple that produced from the conventional solid propellant motors with high oxygen content[3]. The specific impulse is, however, somewhat inferior to that of other ramjet types, due to the fact that the ram-rocket propellant does contain certain amounts of oxidizer, although in much smaller quantities than rocket motors. The inclusion of an oxidizer in addition to the fuel in the propellant composition is necessary, because the combustion of ram-rocket propellants has to be self-sustained, at the first chamber, without the aid of external air[2].

Fuel-rich solid propellants classified into metal-loaded compositions with high smoke levels, carbon compositions with moderate smoke levels and hydrocarbon-fueled compositions with low smoke levels. They characterized by their low combustion temperature, burning rates in the range of few millimeters per second and low specific impulse[3]. Low-pressure combustion for, fuel rich, solid propellants was defined as the interval from 0.1 MPa to 1 MPa, which represent the regime of prime importance for its applicability as a source of partially burned fuel for a ramjet engine[1,4]. The formulations studied within this work represent the low smoke level compositions and were formulated on the basis of polybutadiene pre-polymer (HTPB) as a binder and ammonium perchlorate (AP) as an oxidizer. Further investigation includes system in which burning rate accelerator, copper chromite (CC), added at the expense of the binder[5].

The objective of the present experimental investigation was to determine the flammability limits, combustion efficiency and ballistic properties of such fuel-rich propellant compositions at low pressure according to factors affecting combustion such as oxidizer solid loading, oxidizer particle size distribution through the mean particle diameter of a bimodal system[6] and content of burning rate accelerator. A one-test step method for that investigation (strand burner) used[1,7].

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2 Experimental

2.1 Propellant formulations

The compositions of all tested propellant formulations presented at Table 1. Preparation of the propellants for the test program was made by using a heavy-duty mixer (9×10^{-3} m^3 capacity) with weight of 8 kg per formulation to guarantee the slurry homogeneity. Propellant slurry casting was applied in a carton with standard dimensions 15 cm × 15 cm × 20 cm under vacuum and vibration, then after curing followed by propellant strands preparation and insulation using standard techniques.

The propellant binder was composed of 85.7% HTPB as a main backbone, 12.3% hexa-methylene di-isocianate (HMDI) as a cross-linking agent and 2.0% methyl aziridinyl phosphine oxide (MAPO) as a bonding agent[1,5]. All propellant compositions contained 0.5% carbon black (CB) with 10 μm particle size as an opacifier, which was found to be very important to apply the black body role[1,3]. The base line propellant formulation (A3) consisted of 45% AP with 9.0 μm particles and the particle size variations were investigated through a bi-modal system with AP (64.0 μm)[6].

Table 1 The fuel-rich propellant formulations studied

group	composition	binder/%	AP/% (9 μm)	AP/% (64 μm)	AP average size/μm	CC/%[1)]	CB/%[2)]
A	A1	74.5	25.0	0	9.0	0	0.5
	A2	64.5	35.0	0	9.0	0	0.5
	A3	54.5	45.0	0	9.0	0	0.5
B	B2	54.5	30.0	15	44.5	0	0.5
	B3	54.5	15.0	30	55.9	0	0.5
C	C2	51.5	45.0	0	9.0	3.0	0.5
	C3	48.5	45.0	0	9.0	6.0	0.5

Note: 1) particle size of CC is 0.75 μm. 2) particle size of CB is 10 μm.

2.2 Apparatuses

Propellant linear burning rate and flammability limits were measured by using a strand burner (Crawford bomb) with high accuracy. The combustion efficiency was investigated using standard chemical laboratory facilities. The controlled apparatus (see Fig. 1) under standard environmental conditions, measured the fuel-rich propellant formulations auto-ignition temperature.

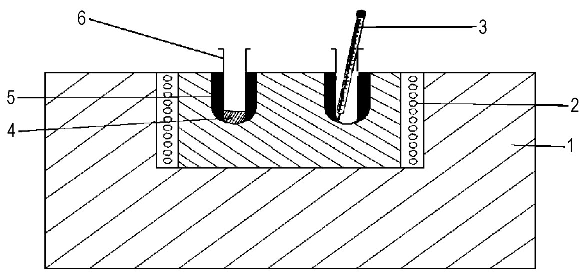

Fig. 1 Schematic diagram for ignition temperature measurement
1—metal block, 2—controlled heater, 3—thermometer, 4—propellant sample, 5—wood's metal, 6—glass test tube

2.3 Measurement methods

Propellant burning rates were measured by using the strand firing technique. Propellant strands, 100 mm length, 10 mm × 10 mm square cross-section, were burned under controlled nitrogen pressures. Ignition of the propellant achieved by a hot wire technique where the propellant surface coated with a compatible pyrotechnique lacquer in which the hot wire was embedded[4]. Burning rate was determined from the burning time of a specified propellant length. The whole measurements conducted at the pressure range from 0.1 MPa to 1 MPa and temperature of +20 ℃. At least 5 samples tested under each condition.

The flammability limits were obtained by discovering the minimum pressure at which the propellant samples combustion continued to the end of the strand without cuffing (low critical deflagration pressure (p_{cr}). At least 3 samples, from the 5 tested samples, should verify combustion sustain for each formulation under each pressure to accept its results[1].

The combustion efficiency was measured by using a quantitative chemical analysis technique over the, propellant strands, after combustion residuals (including carbon soot and virgin unburned propellant spots inside the burner chamber) which were collected for each formulation under each tested pressure. The residuals was swelled by *n*-hexane solvent to separate the binder and exposed to hot water to dissolve the AP then filtered and dried to detect the unsolved matter percentage, which was taken as a measure for the propellant combustion efficiency under a certain pressure regime.

3 Results and discussion

3.1 Ignition temperature

As presented at Table 2, the effect of the formulations on ignition temperature (T_i) was shown at atmospheric pressure and 20 ℃. In group A, it is noted that the higher the solid loading of the oxidizer is, the lower the ignition temperature is. It is because of the increase in the oxidizer volumetric filling through binder matrix microstructure rising the propellant thermal conductivity. While in group B the increasing of the average particle size leads to increase its value due to the decrease of the adjacency between the oxidizer particles. CC addition in place of part of the polymeric binder in group C, leads to T_i remarkable decrease by about 16% for composition containing 6% solid loading, due to the exothermic catalytic reaction at CC-AP interface which increase the sensitivity of AP to heat[7-8].

Table 2 The propellant formulations T_i, C_{ub} and p_{cr} measurements

group	composition	T_i/℃	C_{ub}/%	p_{cr}/MPa
group A	A1	321	69	5[1]
	A2	311	63	0.8
	A3	299	27	0.1
group B	B2	303	33	0.4
	B3	309	56	0.8
group C	C2	274	0~4	–
	C3	252	0~4	–

3.2 Flammability limits

Solid propellants flammability (p_{cr} values shown in Table 2) is a function of a number of parameters. For propellants consisting of the same ingredients, the basic flammability limit presented in terms of pressure versus oxidizer content[7]. Fig. 2 shows the flammability limits of propellants composed of an AP oxidizer of the smallest average particle size (9.0 μm) used in this investigation. The results reveal a distinct limit between sustain and no sustain combustion situations. High pressures are required for sustained combustion when decreasing the AP content[1]. While propellant containing 45% AP could sustain combustion, even at 0.1 MPa (the lowest tested pressure), the propellant having 25% AP did not burn even at 1 MPa. It was recorded that composition A1 started to sustain combustion at 5 MPa[1]. Note that the non-burning compositions ignited and partially burned but could not sustain combustion upon the removal of the ignition wire of the strand burner. The flammability limit trend is hypothesized to be associated with the chemical reaction and heat feedback mechanisms[7]. Propellants with lower AP content exhibit lower flame temperatures resulting in smaller heat transfer to the surface and possibly less extensive reactions. On the other hand, higher pressures cause the gas-phase flame to be hotter, closer to the surface and more extensive[4]. As a result, the heat feedback to the propellant surface enhanced and the combustion more easily sustained.

Influence of the AP particle size was examined using propellants of the same composition (45% AP, no additives) but with different AP particle size distribution of average volumetric sizes as follows: 9.0 μm, 44.5 μm and 55.9 μm. Fig.3 presents the combustion limits in terms of the pressure versus average AP particle size. The larger the particle size the higher the pressure required to sustain combustion. Formulations containing AP particles smaller than about 44 μm could burn even at 0.4 MPa pressure. Decreasing AP particle size in conventional composite propellants known to increase the burning rate[9]. This behavior seems to indicate that, in general, smaller AP particles promote processes (heat transfer, diffusion) establishing more favorable conditions for sustained combustion.

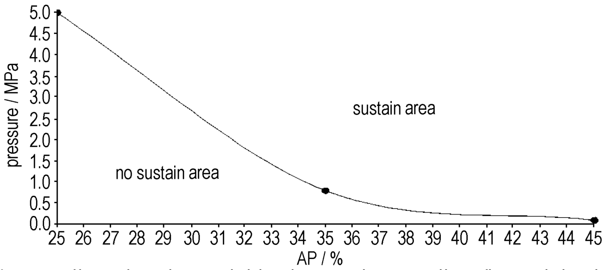

Fig.2 Effect of oxidizer solid loading on the propellant flammability limits

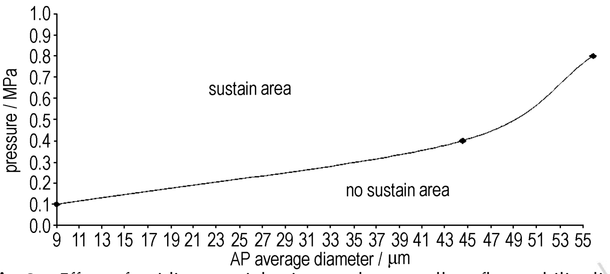

Fig.3 Effect of oxidizer particle size on the propellant flammability limits

3.3 Combustion efficiency

During nearly all test-runs, unburned propellant spots found in the strand burner chamber with different amounts (detected after chemical analysis). This methodology is applicable only for the non-metallic fuel-rich composite propellants. The concentration of the unburned propellant mutter (C_{ub}%) in the combustion residuals was inspected (Table 2), which identified as a sign for the propellant burning completeness under a certain pressure regime. The higher C_{ub}% is, the lower combustion efficiency (100-C_{ub}%).

The results show that the combustion efficiency was very poor (about 31%, 37% and 44% respectively) for composition A1, A2 and B3 and poor (about 73% and 67% respectively) for composition A3 and B2 over the whole tested pressure regime. On the other hand, a complete combustion (about 96% at 0.1 − 0.2 MPa and 100% at 0.4 − 1 MPa) for group C compositions was verified, because CC reduces the activation energy required to start the deflagration reaction overall propellant surface[8]. It was recorded that the combustion efficiency, for a typical solid propellant formulation under a certain pressure regime, marked as "poor" at the interval from 50% to 75%[4].

3.4 Ballistic properties

Effect of propellant composition and different additives on the burning rate level, in general, and on the burning rate dependence on pressure, in particular, investigated. The oxidizer content effect studied using 9.0 μm AP particles ranging from 25% to 45%. Fig.4 shows the trend of increasing the burning rate when increasing AP content at 0.8 MPa and 1 MPa for formulations A2 and A3. There were no results for both the formulations containing 25% AP (even at 0.1 MPa) and 35% AP (at pressures lower than 0.8 MPa). It is clear that the higher the pressure the higher the burning rate. The increase in the burning rate when the oxidizer content increases was demonstrated due to the increase of the oxidizer volumetric solid loading through the propellant microstructure, reaction ability increase to be more exothermic and propellant surface temperature increase over the solid gas interface[1,9].

The oxidizer particle size, distribution, effect on the burning rate shown in Fig.5 for propellants containing 45% AP of average particle sizes ranging from 9.0 μm to 56.0 μm. In general, a monotonic decrease in the burning rate when increasing the particle size was demonstrated in all pressures due to the decrease of the oxidizer burning surface area[6,9]. It is clear that there were no results for formulations B2 and B3 at pressures lower than 0.4 MPa and 0.8 MPa respectively.

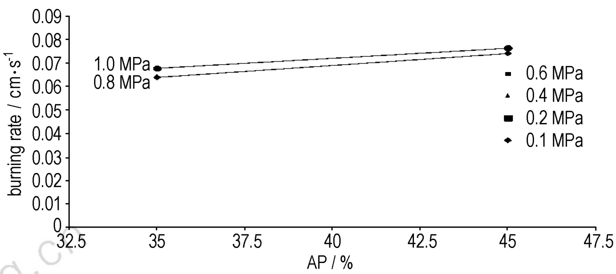

Fig.4 Effect of the oxidizer solid loading on the burning rate

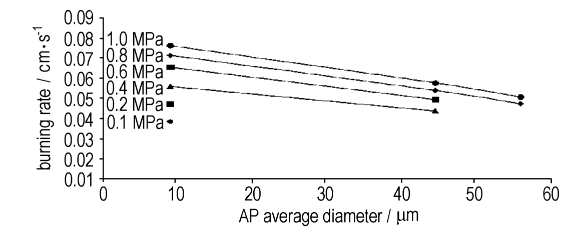

Fig.5 Effect of the oxidizer particle size on the burning rate

The effect of burning rate accelerator CC, with average particle size of less than 1 μm was investigated. The accelerator at fractions varying from 3.0% to 6.0% added to propellant formulations containing 45% AP oxidizer at the expense of the polymeric binder. The 0.75 μm CC exhibited a moderate increase in burning rate for the propellant (Fig.6) due to the exothermic reaction at the CC-AP interface that lowers the oxidizer ignition temperature. In addition, reduces the activation energy required to start the deflagration reaction on the propellant surface. Consequently, increases the reaction rate through the propellant solid-gas interface[1,8].

Fig. 7 shows the burning rate versus pressure correlations for the propellant formulations (except formulation A1, no results). It is clear that this family of fuel-rich propellants follows Vieille burning rate law under the whole regime of 0.1 – 1 MPa and no strange behavior for the burning rate profiles was noticed. Vieille law expressed by the Formula: $r = ap^n$. Where, r is the burning rate, cm · s^{-1}; a is the burning rate pre-exponential factor[1] (cm · s^{-1}. MPa^n); p is the pressure, MPa; n is the pressure exponent index.

As shown in Fig. 8, (except A1), the calculated values for the pressure exponent (n) under the pressure regime from 0.1 MPa to 1 MPa were acceptable and follow the international behavior of change according to propellant formulation[9].

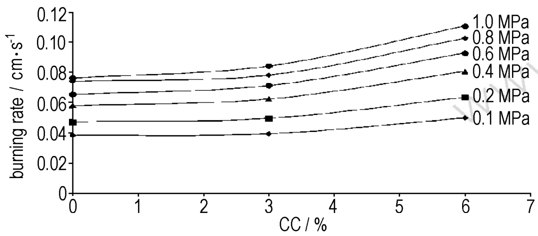

Fig. 6 Effect of the CC solid loading on the burning rate

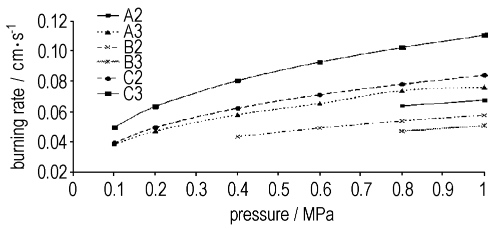

Fig. 7 Burning rate versus pressure correlations for the propellant formulations

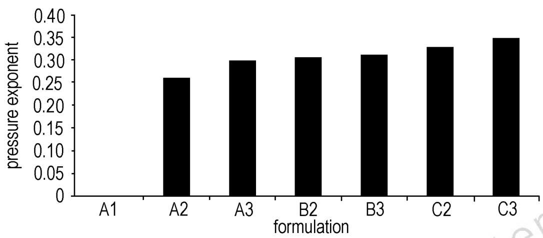

Fig. 8 Propellant formulations effect on pressure exponent

4 Conclusions

The combustion behavior for solid propellants at low pressures is very important and represents a prime importance for its applicability. Combustion envelope of AP/HTPB-based fuel-rich propellants found to be broader for higher pressure value, larger AP contents and smaller AP particle size. Capability of sustaining combustion increased when fine AP sizes of about 9.0 μm and solid loading of about 45.0% used even at atmospheric pressure. Burning rate enhancement demonstrated for higher AP content and smaller AP particle size. The addition of copper chromite (CC) as a burning rate accelerator caused an increase in the burning rate with a significant decrease in the propellant ignition temperature. The combustion efficiency was marked as "acceptable" only for formulations containing CC. It has been established that the Vieille burning rate law for this propellant family may be extended to extremely low pressures.

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少烟富燃复合推进剂低压燃烧特性

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摘　要：研究了 HTPB/AP 富燃复合固体推进剂在 0.1 ~1 MPa 下的燃烧特性。结果表明，高压、高 AP 浓度和较小的 AP 粒子尺寸能促进稳定燃烧，提高燃速和燃烧效率，降低点火温度。亚铬酸铜(CC)作为增速剂能提高整个压力范围内的燃速，6% CC 可降低推进剂点火温度 16%，燃烧效率可达 96%，而未添加 CC 的推进剂配方燃烧效率仅为 31% ~73%。研究表明，在极低的压力下 Vieille 燃速公式对此系列推进剂仍然适用。

关键词：物理化学；复合推进剂；富燃推进剂；燃速；亚铬酸铜

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