



REVIEW

Role of Oxides of Iron on the Combustion of Composite Solid Propellants: A Review

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The effects of iron oxides (α -Fe₂O₃, γ -Fe₂O₃, Fe₃O₄ in the different size ranges from micron to nano) on the combustion of composite solid propellants, also known as hydroxyl terminated polybutadiene/aluminium/ammonium perchlorate (HTPB/Al/AP) systems, are thoroughly reviewed in this work. The effect of the oxides of iron in (i) condensed phase; (ii) sub-surface and surface; (iii) premix flame (gas phase); and (iv) final flame (gas phase) in deflagration zone are also critically reviewed. The effect of catalyst on the lower pressure limit (LPL), upper pressure limit (UPL) and ignition delay is also studied as a part of the combustion phases. It is understood that unlike during the combustion of pure ammonium perchlorate, the role of iron oxides starts its influence on binder system degradation, binder-ammonium perchlorate reactions at surface and HClO₄ decomposition in gas phase. The role of aluminium is to contribute for larger energies in both primary and diffusion flame zone, the heat generated accelerates the surface reactions further. Another interesting topic is nano-oxides of iron, since nanosize contribute for definite increase in burn rate, but the disadvantage of agglomerations both at mixing level and combustion level needs to be addressed. Several strategies are suggested, with the most significant ones being co-precipitation with ammonium perchlorate and the utilization of dispersion agents.

Keywords: Iron oxides, Burn rate, Propellants, Deflagration, Ammonium perchlorate.

INTRODUCTION

Chemical propulsion is a method to derive the energy from the chemical potential of a material. Often this is achieved by chemical reaction called combustion. Two chemical moieties are required for combustion *e.g.* oxidizer (electron acceptor) and fuel (electron donor). Both the rate and energy of the combustion reaction are important in defining the power and sizing of the rocket propellant. This review study focuses exclusively on solid phase propellants, specifically the generic class of hydroxyl terminated polybutadiene/aluminium/ammonium perchlorate (HTPB/Al/AP) based composite propellants. This class has been selected because a majority of widely used solid propellants belong to this category. Today's solid propellant is a composite wherein the oxidizer (ammonium perchlorate, AP) and metallic fuel (Al) in powder form are distributed within a liquid fuel binder (hydroxyl terminated polybutadiene, HTPB) [1-4].

In order to boost the rate of reaction, often combustion modifiers, also called burn rate modifiers/burn rate catalysts are being used to an extent of 2% wt./wt. for augmenting the burn rate by 10% to 60%. Usually, the mixed oxides of transition metals are the candidate materials to act as burn rate modifiers in order to accelerate the ammonium perchlorate decomposition. It is surprising that just two catalysts *viz.*, iron oxide (double oxides of iron (Fe²⁺, Fe³⁺)) and copper chromite ((Cu¹⁺, Cu²⁺), (Cr²⁺, Cr⁶⁺)) have been utilized for ammonium perchlorate breakdown in the rocketry since the introduction of composite solid propellants [5]. India uses copper and chromium oxide combination called copper chromite in the range of 0.15-0.3%. Most of the literature indicates that both copper chromite and iron oxide work on the decomposition of ammonium perchlorate [6]. The impact of these catalysts on the breakdown of the carbonaceous component of the formula, namely the breakdown of polymer (HTPB), has been largely unexplored in the literature.

The purpose of this review is to examine the many theories, models, data patterns and conclusions drawn from the studies conducted by researchers all over the world about the effect of iron oxide on the burn rate of both metallic and non-metallic materials.

Solid propellants: To assess the influence of burn rate catalysts on deflagration combustion, our focus has been exclusively on composite solid propellants. These propellants represent a specific category of deflagration explosives, and our analysis is tailored to understand the effects of burn rate catalysts within this particular context. Propellants are the mixtures of chemical compounds that produce large volume of gas at controlled, pre-determined rates [3]. In the initial years, a composite mixture of carbon (fuel), sulphur (binder) and potassium nitrate (oxidizer) was used in solid propellant rocket motors [7]. During last 60's and early 70's propellants based on either nitrocellulose or on synthetic crosslinked polymeric binders such as polysulphides, polyurethanes or polybutadienes were used. Polymer based rocket propellants, generally referred to as composite propellants, contain crosslinked polymers that act as a visco-elastic matrix for holding a crystalline inorganic oxidizer such as ammonium perchlorate and for providing mechanical strength. Many other substances may be added including metallic fuels, plasticizers, extenders and catalysts to improve the mechanical, storage and ballistic properties [4]. These devices are mostly used for propelling projectiles from firearms, rockets and missile systems.

Evolution of composite solid propellants (CSP): The development of castable composites was started in 1942 at the Guggenheim Aeronautical Laboratory with the formulation of mixture containing 25% (by wt.) asphalt and 75% potassium perchlorate [8]. These were rapidly superseded by a variety of cross-linked elastomer-based propellants with superior mechanical properties and increased available energy, which contained as much as 90% crystalline filler in the polymeric matrix. The most widely used binders include polysulphides, polyurethanes and polybutadienes [4].

Metallized solid propellants refer to solid propellants containing metal powder that has the ability to react with oxygen and oxygen carriers, resulting in the release of heat. In addition to the heat generated per gram of solid propellant, it should have many other useful properties such as storage at ambient conditions, ageing characteristics, friction sensitivity, ignition characteristics, *etc.* Aluminium is virtually the universal fuel for composite propellants. It is available in spherical powders, with small diameters and well suited for high solid loading. Apart from aluminium, some metals like boron, beryllium and lithium have also been used in very specific applications. Because of the increased cost, toxicity, long-term instability and toxic combustion products, the latter fuels lost their applicability [9].

The first solid oxidizer used in composite propellants was potassium perchlorate (KClO_4), which is stable, compatible and relatively insensitive but contributes little energy. Thus, it was later replaced by ammonium perchlorate and is now the most commonly used oxidizer in composite propellants. The high oxygen content, negative energy of decomposition, ignition

temperature, crystal transformations before decomposition made this possible. The AP-HTPB composite mixtures containing aluminium powder are the most frequently used solid rocket propellants worldwide. Similarly, ammonium perchlorate is oxidizer rich and can sustain self-deflagration above 20 bar. When ammonium perchlorate of size $40\ \mu$ mixed with $300\ \mu$ powder, *i.e.* bimodal ammonium perchlorate, the burn rate is higher than the burn rate of ammonium perchlorate with single size. One additional benefit of ammonium perchlorate is its tendency to undergo sublimation prior to decomposition. This characteristic indicates that the combustion of ammonium perchlorate is limited to either the solid phase, the gas phase or both. The uncertainty due to the presence of liquid/melt phase is thus eliminated. Previously, ammonium nitrate was considered as an environment-friendly alternative to ammonium perchlorate, because of its low cost, low sensitivity and absence of chlorine. However, its multiple crystal phase transitions at low temperatures along with volume expansion preclude its use. At 32.1% it undergoes phase change, which is accompanied by a large volume change [1-4].

Burn rate catalysts and their role in solid propellant combustion: The combustion behaviour of composite solid propellants (CSP) is generally characterized by the burn rate, which is a steady linear regression rate of the burning surface. The factors that affect combustion kinetics also influence burn rate. Combustion processes can be seen as gas-solid interactions simply because the byproducts are present in the gas phase. Therefore, the kinetics are typically influenced by gas pressure, composition and temperature as well as solid phase temperature and composition. If the combustion reaction occurs partially in solid phase and partially in gas phase, then surface area and relative rate constants at respective temperatures also affect the burn rate. Burn rate is considerably influenced by the pressure, as given in Vieille's law, $r = ap^n$, where r is the burn rate, p is the pressure and a , n are constants; which depend on formulation, temperature, particle size distribution, packing fraction, heat transfer characteristics, rate of sub-surface reactions. The value of n is between 0.3 and 0.7, which is common in the well-developed formulations [9]. Both condensed phase and gas phase reactions can be catalyzed by the catalysts. As a result of their ability to facilitate electron acceptance and donation, transition metal oxides (TMOs) promptly emerged as the catalysts of choice. In particular, several characteristics have contributed to the significance of their presence [7], for example, (i) metal components in TMO can exhibit variable valency or oxidation states; (ii) catalytic activity results from physical contact; the reaction ceases when particles no longer have an oxidizer-additive interface; (iii) gaseous product distribution may be altered by some catalytic agents; (iv) ammonium perchlorate propellant systems often use iron oxides as catalysts, since the ferric-ferrous pair may play a pivotal role in the redox-cycle that drives combustion catalysis by iron compounds; and (v) burn rate depends on catalyst concentration, surface area and state of aggregation.

Catalysts are known to affect the combustion of composite solid propellants (CSP) and its components—the oxidizer and the binder. Several reviews in this field have been published by

various groups, including Hall & Pearson [8], Jacobs & Whitehead [6], Keenan [10], Kishore & Sunitha [5], Boldyrev [11], Shalini & Dave [12], Chen *et al.* [13] and Vara *et al.* [14]. Changes in the rate of combustion and breakdown of CSP and its components can be facilitated by catalysts known as transition metal oxides (TMO), such as Fe₂O₃, MnO₂, Ni₂O₃, copper chromate, *etc.* [5]. The concentration of these catalysts is another important aspect in their effectiveness [15]; the concentration should be such that it does not alter the propellant composition and must be as low as possible, so that the propellant energetics is not affected. The precise mechanism by which the catalysts influence the breakdown and combustion of CSP remains unclear. Nevertheless, it is widely acknowledged that the interaction between NH₃-HClO₄ (early breakdown products of ammonium perchlorate) and HClO₄-fuel leads to an increased heat release on the surface of catalyst [16,17]. Consequently, the activation energy of the primary flame reaction decreases and as a result burn rate value increases [18]. The available literature mostly concerns mechanistic studies on the action of catalyst on the decomposition and combustion behaviours of non-metallized and metallized propellant formulations.

Role of oxides of iron on the decomposition of composite solid propellants: A composite solid propellant (CSP) refers to a physical mixture of solid particles and a liquid polymer, sometimes referred to as a binder. Primarily, the liquid polymer should be selected based on its wetting properties with respect to the solid particles thereby achieving the acceptable structural properties with good ageing characteristics. In addition, the polymer should not melt during the combustion. After the possibilities for polymers have been frozen, the one with the lowest liquid percentage and the maximum solid loading becomes the clear choice. Therefore, in all decomposition studies, the percentage of liquid remains constant. The liquid component typically comprises the fundamental polymer, plasticizer, curing agent and additional liquid additives designed for modifying the structural characteristics. The solids loading refers to the precise mixture of metallic fuel and oxidizer. It is also a possibility that certain formulas do not contain any metallic fuel. The mutual ratio of oxidizer and fuel (O/F) depends primarily on the maximization of specific impulse although the factors such as processability, castability and ageing need to be considered before final decision. Particle size of oxidizer and fuel also make the difference. The proper adjustment of particle sizes and the percentages should finally take into account the processability. Since CSP is directly used in the rockets, a few studies are oriented to combustion at rocket conditions, *i.e.*, adiabatic conditions at high pressures usually ranging from 30 to 70 atm. The requirement of 30 atm also stems from the need to avoid self-quenching characteristic of ammonium perchlorate. This characteristic is denoted as lower pressure limit (LPL) point at which ammonium perchlorate combustion continues. An increase in occupancy time of reactants and intermediates at both the surface and gas phase is a direct consequence of the applied pressure.

Effect of oxides of iron on the combustion of non-aluminized composite propellant: Wise *et al.* [19] studied the effect of ferric oxide on the pelletized ammonium perchlorate

without binder and monitored the condensed phase reactions, ignition and deflagration of ammonium perchlorate by measuring thermal diffusivity, burn rate and ignition characteristics. They ensured the outward radial regression for burn rate estimation. Moreover, it was concluded that (i) the ignition and steady-state burning happens not only in the gas phase but also in the condensed phase which is called homogeneous reactions within solid; (ii) formation of visible flame during ignition is the result of gas phase reactions and the generation of gas phase reactants is the rate controlling step; (iii) as the pressure increases the rate of generation of the reactants increases thereby these conditions trigger the ignition; and (iv) deflagration on the other hand doesn't depend on the condensed phase reactions since the heat required for condensed phase reactions doesn't match with the recession rate of surface.

The location of action of burn rate catalysts in the combustion of CSP was studied by Pittman Jr. [20]. He used CTPB as binder with a solid loading of ~70% and concluded that location of catalyst action is in the gas phase only and ferric oxide will not influence the condensed phase reactions such as binder decomposition, phase transition of ammonium perchlorate, partial decomposition of ammonium perchlorate into HClO₄ and NH₃. Another work by Kishore *et al.* [21] applied ammonium perchlorate/polystyrene (AP/PS) system at two different concentrations of ferric oxide. The findings of the study suggest that the aforementioned ratios exhibit an upward trend until a specific concentration of ferric oxide is reached, after which they subsequently decrease. The decrease in the rate of combustion was attributed to the decrease in the amount of ammonium perchlorate. The relationship between catalyst concentration and the combustion of CSP is consistent with the impact observed in the combustion of pure ammonium perchlorate. However, no comprehensive elucidation of the reaction mechanisms has been provided. Subsequently, a further publication authored by the same individual [22] attempted to provide a more comprehensive elucidation of the underlying reason. It was believed that the redox potential of the oxides may serve as an indicator of the electron transport mechanism. Their investigations revealed that the burn rate is inversely proportional to the redox potential. Based on this data, the probable

reaction as $\frac{1}{3}\text{Fe}_3\text{O}_4 + \frac{1}{12}\text{O}_2 \longrightarrow \frac{1}{2}\text{Fe}_2\text{O}_3$ was suggested. The

oxygen is generated as a consequence of the decomposition of perchloric acid, similarly, the synthesis of iron perchlorate occurs through the chemical reaction between ferric oxide and ammonium perchlorate. As a whole, they decrease the energy required for breakdown. In other words, it can be inferred that they are indirectly indicating that presence of ferric oxide has an impact on processes occurring in both the gaseous phase and at the sub-surface/surface level.

In 1979, Kishore & Sunitha [5] reported a comprehensive review of prior research pertaining to the combustion of ammonium perchlorate in combination with various binders such as HTPB, CTPB and PS. Additionally, they also examined the influence of ferric oxide on this combustion process (Table-1). The classification of these substances is based on their support

TABLE-1
LOCATION OF CATALYTIC ACTIVITY [Ref. 5]

Sub-surface reactions	Surface reactions	Gas phase primary flame	Gas phase diffusion flame	Ref.
No	No	Yes	Yes	[20]
No	No	Yes	Yes	[22]
No	No	–	–	[23]
No	Yes	–	Yes	[24]
Yes	Yes	–	Yes	[17]
No	Yes	–	Yes	[25]
No	Yes	–	Yes	[26]
No	No	–	Yes	[27]
No	Yes	–	Yes	[28]
No	No	–	Yes	[29,30]
No	Yes	–	Yes	[31]
No	Yes	–	Yes	[32]
No	Yes	–	No	[33]
Yes	Yes	–	Yes	[34]
Yes	Yes	–	Yes	[35,36]

for sub-surface reactions (AP), surface reactions (binder-AP), gas phase main flame and gas phase diffusion flame. Additionally, they also summarized the effect on lower pressure limit (LPL) and upper pressure limit (UPL) as described in Table-2.

Krishnan & Jeenu [41] studied the effect of catalyst on the AP/HTPB composite solid propellant (CSP). The experimental findings suggest that the emission of glowing particles was observed across all tested pressure conditions. When the pressure of the gas phase flame reaches below 0.2 bar, it gradually diminishes and eventually ends up disappearing. A smouldering surface displaying a bright orange luminescence devoid of a gaseous phase combustion was identified, which is not observed with CTPB/AP/Fe₂O₃. The reason is attributed to the exothermic decomposition of HTPB in the sub-surface and surface without a gas phase flame. Moreover, the burn rate pressure exponent exhibits a larger value and is consistent with the principles of granular diffusion flame theory. This can be attributed to the predominance of the premixed flame component within the overall gas phase region. The same authors [42] tried to model the surface reactions theoretically and compared with the earlier studied models *e.g.* Beckstead-Derr-Price (BDP) model [43] and the extensions of this BDP model one by Cohen *et al.* [44] for higher pressures (10-100 bar) and Beckstead *et al.* [45] for low pressures (0.03-1 bar). These models are insensitive to particle size distribution (PSD) of ammonium perchlorate since they assumed constant surface heat release. Both PSD

of ammonium perchlorate and catalyst influence burn rate from the lowest pressure to rocket operating pressures. Sambamurthi & Price [46] suggested the catalyst decompose, evaporate, leave surface or adhere to receding surface during the advent of flame front, however catalyst don't influence binder pyrolysis [47]. Similarly, Jones & Strahle [48] suggested that catalyst don't promote heterogeneous reactions of gases with binders or modify binder pyrolysis but promote gas phase at ammonium perchlorate-binder interface. But, catalyst can increase the burn rate by contacting with ammonium perchlorate particles and promote diffusion of ClO₄⁻ towards catalyst [49].

Chakravarthy *et al.* [50] classified the mechanisms of catalyst effect into 11 types *viz.* (a) physical effect of iron oxide accumulated on the surface getting heated up from the flame and aids binder regression by direct contact; (b) effect of binder melt flow behaviour, physically or chemically; (c) catalysis of binder thermal degradation at urethane linkages in condensed phase near 2-7 MPa pressure; (d) enhanced near-surface breakdown of heavy fuel molecules; (e) action in gas phase by modifying the gas phase reactions by chloride derivatives of catalyst (f) heterogeneous gas phase exothermic reaction between catalyst and HClO₄; (g) gas phase and/or heterogeneous reactions occur in the holes between the fuel and ammonium perchlorate; (h) catalysis of same process in the vicinity of ammonium perchlorate-binder interface; (i) the process of catalyzing the breakdown or deflagration of ammonium perchlorate through proton or electron transfer; (j) action in condensed phase ammonium perchlorate binder interfacial surface, altering decomposition products of ammonium perchlorate + binder and catalyzing HClO₄ eventually promote binder degradation; and (k) formation of metal perchlorates/metal perchlorate amines. The most likely catalytic mechanism is the occurrence of exothermic reactions near or directly on the surface, specifically along the contact lines between the oxidizer and binder. These reactions become major source of heat release and presence of reactive fuel and oxidizer species. They are influenced by particle size and %ammonium perchlorate in the formulation.

In their study, Ishitha *et al.* [51] conducted a comprehensive survey to elucidate the catalytic mechanisms in CSP and classified ammonium perchlorate catalyst mechanisms into three broad classes according to the types of active sites. For example, ammonium perchlorate and binder are both reacted by the catalyst; the catalyst is only effective with ammonium perchlorate and catalyst is only effective on binder. There are few proposed mechanisms: (i) promotion of HClO₄ and fuel reactions; (ii) promotion of decomposition products of HClO₄

TABLE-2
EFFECT ON AP DEFLAGRATION PRESSURE [Ref. 5]

Effect on LPL	Effect on UPL	Remarks	Ref.
Reduces	–	–	[37]
Increases in LTD zone	–	Reduces LPL if heat feedback from gas phase reactions is higher than exothermic reactions on the surface. Usually this happens at HTD zone.	[38]
Increases in LTD zone	–	Supports Friedman's <i>et al.</i> work [38]	[39]
–	–	Catalyst that promote decomposition may or may not necessarily promote deflagration because the temperature of deflagration is different from decomposition studies, there exists thermal and concentration gradients in the deflagration phase and either the liquid layer is present or absent.	[40]

and fuel; (iii) accelerating the electron transfer process; (iv) catalyzing the heterogeneous reactions; (e) catalyzing homogeneous reactions in gas phase; (f) allowing the formation of metal-amine complex; (g) promoting the condensed phase reactions; (h) promoting only gas phase reactions; (i) promotes reactions in diffusion process; and (j) accelerating the oxidizer binder interfacial.

In each category various mechanisms were proposed with few disagreements. For example, Vorobeva *et al.* [52] disagreed with the mechanisms that have been investigated for the purpose of speeding up condensed phase processes. Decomposition of perchloric acid, ammonium perchlorate and deflagration of ammonium perchlorate are the three catalytic mechanisms proposed under the category 2. Similarly, Komarov [53] and Bakhman [31] are in disagreement with the decomposition of perchloric acid as a possible mechanism. Under category 3, two mechanisms were proposed namely promoting the oxidation of binder and catalyzing the binder. However, the mechanism of catalyzing the binder is in disagreement [5,15,20,48]. Many of these observations were investigated through DTA/TG-DSC studies although few on burn rates of sandwich propellants and propellants. Nevertheless, they studied the catalytic mechanism by investigating the thermal conductivity, thermal diffusivity, thermal penetration thickness (ratio of thermal diffusivity and burn rate) and pressure index. Higher thermal conductivity means lesser availability of heat at the surface and thus reduced binder melt flow over the surface. Their hypothesis suggests that the catalyst restricts the expansion of surface binder melt flow, hence increasing the inflow of reactants that enter the gaseous phase during ammonium perchlorate condensed phase reactions.

In literature, the impact of micron-sized ferric oxide on the composition of CSP were also investigated. Nano-sized catalysts, on the other hand, have been the subject of research on CSPs since 2006. The impact of nanocatalyst on the rate of combustion, elucidates its underlying reaction mechanism and explores methods to minimize nanoparticle aggregation. Initially, α -Fe₂O₃ nanoparticles in ammonium perchlorate breakdown experiments were synthesized using the hydrothermal method.

The investigations conducted by Patil *et al.* [54] in 2006 possess two distinct characteristics that set them apart (i) nano-ferric oxide is utilized for investigating CSP combustion and (ii) α -Fe₂O₃ utilized in this study is synthesized by an electrochemical process, which distinguishes it from previous research. The propellant used in this study contains 85% ammonium perchlorate and 15% binder (HTPB). Nano-ferric oxide increased the activation energy from 143.8 kJ/mol to 181.5 kJ/mol, along with the corresponding increase in frequency factor from 3.6×10^{10} to 5.77×10^{10} (5 K/min heating rate). The observation is more or less same at all heating rates from 5 to 25 K/min. The simultaneous increase in activation energy along with frequency factor is attributed to stronger interaction between ammonium perchlorate and HTPB followed by increase in reactant concentration at the catalyst surface. It was concluded that nano-Fe₂O₃ absorbs gaseous reactant molecules present on the surface and catalyzes the reaction leading to the reduction in the heat deflection temperature (HDT).

Kohga [55] studied the effect of ammonium perchlorate particle size and ammonium perchlorate content on the combustion of CSP using nano-ferric oxide and found that nano-ferric oxide reduces the minimum or lower limit of ammonium perchlorate percentage to sustain burning, secondly the reduction in ammonium perchlorate particle size reduced the HTD to a significant temperature of 540 K. In 2010, Fujimura *et al.* [56] studied the efficiency of catalyst as a function of size and surface area of nano-ferric oxide on burn rate of ammonium perchlorate/HTPB composite solid propellant. It was found that as specific surface area increases or particle size decreases the burn rate increases and goes to asymptotic. The rate determining step in this process is the diffusion of ammonium perchlorate and HTPB breakdown products.

In another work, Isert *et al.* [57] used ammonium perchlorate/HTPB propellant containing 20% (binder), 0.25% ferric oxide and ammonium perchlorate as bimodal (400, 20 μ). The encapsulated nano-ferric oxide was prepared using solvent-non-solvent technique with fine ammonium perchlorate. They observed that the catalyst decreases the ignition duration of ammonium perchlorate crystals when present in a coarse form. Nevertheless, this phenomenon disappears to exist at high pressures. Additionally, the introduction of a catalyst does not yield any apparent modification in the configuration of the flame. But alterations in pressure do lead to variations in the flame structure. Sharma *et al.* [58] obtained hexagonal shaped nano-ferric oxide using green method from the neem leaves (*Azadirachta indica*) and studied its effect on CSP combustion. In addition to static TG and monitoring ignition delay at 360-420 °C using the tube furnace technique, the TG-DSC analysis was conducted at a heating rate of 10 K/min with HTPB based CSP + 1% nano-ferric oxide. These results indicated that nano-ferric oxide affected the thermal decomposition of pure ammonium perchlorate on par with other types of ferric oxides. Both low-temperature decomposition (LTD) and high-temperature decomposition (HTD) were influenced from 315 to 295 °C and 445 to 370 °C, respectively indicating that the green synthesized nano-ferric oxide is better than those prepared with other methods. The burn rate was also significantly increased from 1.22 to 2.34 mm/s, since nano-ferric oxide enhanced the condensed phase reactions during the combustion of CSP as also the acceleration of electron flow caused by nano-ferric oxide substantially transforms the NH₄⁺ and ClO₄⁻ ions to NH₃ and HClO₄, respectively. Isothermal TG analysis at 300 °C confirmed the 45% mass loss, which results in the quick decomposition process due to the high temperature and fast heating, as evidenced by the ignition delay kinetics. Moreover, the adsorption of gaseous products of dissociation of ammonium perchlorate is promoted by the presence of green synthesized nano-ferric oxide.

Recently, Kohga & Togo [59] examined the enhancement of ammonium nitrate combustion by introducing ammonium perchlorate and nano-Fe₂O₃. It was observed that when the percentage of ammonium perchlorate in the mixture of ammonium perchlorate and ammonium nitrate increases, the burn rate index reaches its highest point at around 0.4. Moreover, the thermogravimetric analysis showed that ammonium per-

chlorate and ammonium nitrate undergo separate decomposition processes at their respective characteristic temperatures of 634 K and 535 K. In the temperature range of 535 K to 634 K, there exists a self-quenching area despite the presence of nano-ferric oxide. This finding further supports the idea that the presence of ammonium perchlorate does not alter the combustion of ammonium nitrate. Additionally, the requirement for decomposition at 634 K is diminished when the particle size distribution (PSD) of ammonium perchlorate is decreased from a coarse size of 63 μ to a finer size of 3 μ .

In continuation of their work, Kohga *et al.* [60] studied the effect of different particle sizes of ammonium perchlorate (40, 0.5, porous 2.5 μ) at various concentrations (below 1% and 4%) of nano-ferric oxide. Upon observation, the relationship between percent augmentation (R) and pressure exhibits an initial increase up to a certain pressure followed by a subsequent decrease. Additionally, when the particle size of nano-ferric oxide is changed, the surface temperature augmentation (χ) is significantly enhanced within the range of 1-4% of ammonium perchlorate. The effect was ten times larger with ammonium perchlorate with a coarse surface, whereas it was only three times larger with ammonium perchlorate with a sub-micron porous surface. Based on the above mentioned results, the authors found that the burn rate index increases when the temperature gradient in the gas phase at the burning surface increases with pressure, resulting in a reduction in flame length. On the other hand, the burn rate index decreases when the temperature gradient and length in coarse ammonium perchlorate do not decrease significantly. However, in fine and porous ammonium perchlorate, nano-ferric oxide directly reduces the length of both the primary and diffusion flames at the primary flame. Moreover, the critical diameter of ammonium perchlorate, at which the change from reduction in flame length occurs, was around 19 μ . Therefore, in practical terms, when ammonium perchlorate is greater than 19 μ , it behaves similarly to coarse ammonium perchlorate in relation to flame structure. At the same time, when ammonium perchlorate is less than 19 μ , it behaves like fine ammonium perchlorate.

Effect of oxides of iron on the combustion of aluminized composite propellant: Burnside [26] was the first person who extensively studied the role of ferric oxide on the combustion of aluminized CSP in year 1975. The weight percentage of the CSP composed of HTPB binder, aluminium, ammonium perchlorate and ferric oxide contains 12% HTPB binder, 10% aluminium, 78% ammonium perchlorate and 0.4-2% ferric oxide with modifications made in ammonium perchlorate. Similarly, the weight percentage of the CSP composed of CTPB binder, aluminium, ammonium perchlorate and ferric oxide, which consists of 14% CTPB binder, 5% aluminium, 81% ammonium perchlorate and 0.1-1.0% ferric oxide, with adjustments made in ammonium perchlorate. The binder and aluminium remain consistent, while the particle size of ammonium perchlorate was varied between 400, 200, 7-11 and 10 μ , whereas the surface area of ferric oxide ranges from 3 to 26.4 m²/g. The results indicate that ferric oxide surface area is more significant at high fine ammonium perchlorate levels than low fine ammonium perchlorate levels. Catalysis takes place in the primary diffusion

flame at ammonium perchlorate binder interface. Without a catalyst the flame kinetics follow a simple power function in pressure whereas with catalyst, it follows a heterogeneous catalysis such as Langmuir-Rideal mechanism.

Yoo *et al.* [61] compared the effect of ferric oxide on the combustion of non-aluminized and aluminized CSPs. In aluminized CSP, aluminium was adjusted in ammonium perchlorate varied from 0-20%. The researchers collected data on burn rate and pressure exponent by varying the particle size of ammonium perchlorate and the concentration of ferric oxide. The findings demonstrated that in non-aluminized CSP, an increase in the percentage of ferric oxide resulted in both an increase in burn rate and pressure exponent. This increase reached saturation at a level of 0.8%, which can be attributed to a reduction in the amount of energy transferred from the primary flame and diffusion flame to the burning surface area. Herein, ferric oxide acts in primary flame kinetics and thus effect burning rate at low pressure rather than at higher pressure. Upon the addition of aluminum, the exothermic energy resulting from aluminum oxidation is of such magnitude that it surpasses all other minor contributions. Hence, the effect of catalyst becomes lesser in aluminized propellants, burn rate as well as pressure exponent decreased due to the presence of aluminum.

Ma [62] studied the effect of pure ferric oxide and ferric oxide co-precipitated with ammonium perchlorate. In case of ferric oxide co-precipitated with ammonium perchlorate, the pressure exponent remained constant irrespective of the percentage unlike others. Since ferric oxide cannot enter the gas phase but instead builds up on the surface or subsurface in the form of a layer, an increase in burn rate that occurs when two phases were physically mixed is thought to be due to processes occurring below the surface. On the other hand, co-precipitated ferric oxide prevents such accumulation because ferric oxide already reacts with decomposition products of ammonium perchlorate.

Wang *et al.* [63] studied the catalytic activity of nano-ferric oxide on aluminized CSP (binder/aluminium/ammonium perchlorate/ferric oxide). At 11 MPa, the burn rate increased from 9.26 to 14.94 mm/s. The pressure exponent also increased from 0.4225 to 0.4886, which implies that the catalyst works on the thermal decomposition of ammonium perchlorate. Pang *et al.* [64] studied the effect of nano-ferric oxide on the combustion of CSP with the formulation HTPB/aluminium/ammonium perchlorate/plasticizers/ferric oxide). Aluminum powder is micron sized, ammonium perchlorate is bimodal (particle sizes of 105-147 μ and 1-5 μ prepared by grinding) and average particle size of ferric oxide was 48 nm (d₅₀). According to their findings, nano-ferric oxide increases the burn rate, lowers the pressure exponent (tested between 1 and 15 MPa) as well as the explosion heat. Agglomeration and aggregation events close to the burn surface are indicative of a multi-flame structure, according to the flame morphology.

Demko *et al.* [65] prevented the agglomeration of nanoparticles by producing them directly in the binder utilizing sol-gel procedures. At the same time, the binder functions as a de-agglomerating agent. The burn rate exponent was enhanced, but the burn rate was decreased, by the *in situ* growth of nano-

ferric oxide in both aluminized and non-aluminized propellants. The decrease in burn rate was ascribed due to the lack of optimization in the formulation's surface chemistry of iron oxide particles. Marothiya *et al.* [66] also studied the effect of nano-iron oxide on aluminized CSP by adding nano-iron oxides embedded on ammonium perchlorate and compared with micron-iron oxide embedded on ammonium perchlorate. The researchers determined that the approach of including a catalyst into ammonium perchlorate to address the problem of particles clumping together resulted in a positive outcome by enhancing the rate of combustion. This happened due to the relatively higher proximity of iron oxide to ammonium perchlorate.

Another strategy for de-agglomeration applied by Budhwar *et al.* [67] is to disperse the nano iron oxide using coconut oil. Coconut oil dispersion increased the BET surface area from 34.2 to 45.6 m²/g with a corresponding decrease in particle size from 33.4 to 25.1 nm. Upto 0.5% the capped nano-iron oxide resulted in higher burn rate, while at 0.75%, the burn rate started decreasing and hence stopped further estimation of burn rate. The fundamental characteristic of iron oxide is a tendency of rise followed by decline with an increase in the percentage of iron oxide. However, their experiments showed that nanoparticles physically dispersed is further increasing the burn rate upto 1.5% and the corresponding burn rate is 13.23 mm/s. The TG-DSC analysis of propellant samples with 0.25% iron oxide indicates that the catalyst acts in lowering the HTD temperature. The addition of catalyst helps in increasing the ammonium perchlorate mass loss and lowering the HTD peak to produce gases. Thus, the capped iron oxide is more effective in producing the gases.

Maggi *et al.* [68] studied the effect of two different haematite batches A and B from the same supplier and tried to compare them. The TG-DSC of propellant samples indicates A=B with respect to HTD temperature reduction. Both A and B samples have somewhat lower pressure exponents and marginally superior burn rate enhancements, with A sample emerged out on the highest with 0.28%. It indicates that there is no gross change in the decomposition mechanism. The quenched surfaces found the presence of aluminum to an extent of 26% and 41% implying aluminum accumulation on the surface. If there is genuine aluminum accumulation, it alters the reaction process by reducing the evaporation of HCl, resulting in an elevated concentration of ammonia. The elevated levels of ammonia result in the formation of nitrogen in the combustion byproducts. Similarly, Rekha *et al.* [69] also studied the effect of iron oxide obtained from two different sources with change in purity (68.2, 65.5%) and significant difference in bulk density (0.65, 0.107), particle size (0.68, 1.43) and specific surface area (4.5, 71.2 m²/g). Two types of ammonium perchlorate was used, bimodal (300, 60 μ) and trimodal (300, 60, 6 μ) to an extent of 67%. The results indicate that burn rate increases with % iron oxide whereas the pressure exponent decreases. Trimodal ammonium perchlorate couldn't change the burn rate but decreased the pressure exponent value. It was concluded that incorporation of iron oxide eliminates the need for going to trimodal ammonium perchlorate, thus, iron oxide from source B was better than that of source A.

While it is beyond the focus of this review article, it is important to acknowledge the review conducted by Liu *et al.* [70]. The review examined various iron-based compounds and their synthesis techniques, along with their characterization as catalysts suited for the propellant applications. These compounds include micro-octahedron, nano α-Fe₂O₃ with different shapes, Fe₂O₃ precipitated on amorphous carbon and graphene, as well as spinels of copper, magnesium, manganese, zinc, nickel and cobalt. They indicated that these catalysts have a tendency to migrate during curing and storage process which is not desirable. Migration is, according to them because of the size proximity to ammonium perchlorate and binder and concentration gradient due to agglomeration. They proposed that the solutions for delaying migration should be developed in the future.

Conclusion

In conclusion, this work serves as a comprehensive review delving into the significant role of iron oxides in the combustion of composite solid propellants, particularly those involving hydroxyl terminated polybutadiene (HTPB), aluminum (Al) and ammonium perchlorate (AP) systems. The impact of iron oxides (α-Fe₂O₃, γ-Fe₂O₃ and Fe₃O₄) ranging from micron to nano-meter scales is discussed in this review article in different burning scenarios, including the condensed phase, subsurface and surface reactions, pre-mix flame in the gas phase and final flame in the deflagration zone. Notably, the focus excludes detonation studies, centering on the effects of catalysts on low-pressure laminar (LPL), upper pressure limit (UPL) and ignition delay within different combustion phases. Unlike the combustion of pure ammonium perchlorate, the influence of iron oxides extends beyond simple ammonium perchlorate decomposition. It encompasses binder system degradation, reactions at the binder-ammonium perchlorate interface and HClO₄ decomposition in the gas phase. A significant finding is the recognition that aluminum plays a large role in the release of energy in the main and diffusion flame regions, where the surface processes are sped up by the heat produced. Moreover, the incorporation of nano-sized iron oxides is explored, revealing a definite increase in burn rate. However, challenges like agglomeration at mixing and combustion levels require careful consideration. Strategies such as co-precipitation with ammonium perchlorate and the utilization of dispersing agents are proposed to address these challenges. As this review highlights the application of nano-sized catalysts in propellant compositions is an evolving area, presenting avenues for further research and development. The comprehensive insights provided herein contribute to a deeper understanding of the complex interplay between iron oxides and the combustion dynamics of composite solid propellants, paving the way for advancements in propellant design and performance optimization.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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