



King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



REVIEW

Solid propellants: AP/HTPB composite propellants[☆]



Shalini Chaturvedi, Pragnesh N. Dave^{*}

Department of Chemistry, Krantiguru Shyamji Krishna Verma Kachchh University, Mundra Road, Bhuj 370 001, Gujarat, India

Received 23 April 2013; accepted 31 December 2014

Available online 8 January 2015

KEYWORDS

Solid propellants;
AP;
HTPB;
Burning rate;
Combustion

Abstract In this article we mainly discuss about AP/HTPB composite solid propellants. Classification, components, properties, burning rate and ignition behavior of propellants are mentioned here. Combustion of AP monopropellant, HTPB and AP/HTPB is discussed in detail.

© 2015 The Authors. Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Contents

1. Introduction	2062
2. Components and properties	2062
2.1. Oxidizer	2062
2.2. Metal fuel	2063
2.3. Binder	2063
2.4. Modifier or Catalyst	2063
2.5. Plasticizer	2063
2.6. Curing agent	2063
2.7. Additive	2063
3. Classification	2063
3.1. Homogeneous solid propellants	2063
3.1.1. Single-base propellants	2063
3.1.2. Double-base propellants	2064
3.1.3. Composite modified double base propellants	2064

^{*} Corresponding author.

E-mail address: pragnesh7@yahoo.com (P.N. Dave).

[☆] This review discusses about AP/HTPB composite solid propellants. Classification, components, properties, burning rate and ignition behavior of propellants are mentioned here. Combustion of AP monopropellant, HTPB and AP/HTPB is discussed in detail. Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

<http://dx.doi.org/10.1016/j.arabjc.2014.12.033>

1878-5352 © 2015 The Authors. Published by Elsevier B.V. on behalf of King Saud University.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

3.1.4. Triple-base propellants	2064
3.2. Heterogeneous solid propellants	2064
3.2.1. AP-composite propellants	2064
3.2.2. Ammonium Nitrate based Propellants	2064
3.2.3. Nitramine composite propellants	2064
3.2.4. Minimum-signature (smokeless) propellants	2065
4. Combustion	2065
4.1. Combustion of AP Monopropellant	2065
4.2. Pyrolysis of HTPB Binder	2065
4.3. Combustion of AP/HTPB Propellant	2066
5. Burning properties.	2066
6. Ignition	2066
7. Conclusion	2067
Acknowledgments	2067
References.	2067

1. Introduction

Solid propellants are mainly used in gun and rocket propulsion applications (Singh et al., 2009a, 2011; Chaturvedi and Dave, 2011a,b). They are very energetic and produce high temperature gaseous products on combustion. The high material density of solid propellants leads to high energy density (The energy produced by a unit mass of a propellant is called its energy density) needed for producing the required propulsive force. Propellants in onboard rocket are burned in a controlled way (deflagration) to produce the desired thrust. A solid propellant consists of several chemical ingredients such as oxidizer, fuel, binder, plasticizer, curing agent, stabilizer, and cross-linking agent. The specific chemical composition depends on the desired combustion characteristics for a particular mission. Solid propellants are often tailored and classified by specific applications such as space launches, missiles, and guns. Different chemical ingredients and their proportions result in different physical and chemical properties, combustion characteristics, and performance (Beckstead et al., 2007).

Ammonium perchlorate (AP)-based composite propellants have been a workhorse in the field of solid rocket propulsion for more than five decades. This type of propellant typically contains a multi-modal distribution of AP (NH_4ClO_4) grains (~ 20 to 200 mm) embedded in the hydroxyl-terminated polybutadiene (HTPB) matrix. The physiochemical processes that occur during the combustion of AP/HTPB propellant include condensed-phase heating, degradation of AP and HTPB, melting and surface pyrolysis, and gas-phase reactions. The flame structures and burning behavior depend on several factors, such as propellant composition, AP grain size, initial and ambient conditions, and propellant morphological configuration.

The combustion characteristics of AP-based composite propellants were extensively studied during the 1960s and 1970s under various rocket-motor development programs. Several literatures reported earlier on the state of the knowledge up to the 1980s were written by Kishore (1979) and Ramohalli (1984) etc. After lots of research efforts in the following years, AP based propellants on account of the progress in experimental diagnostics and a numerical simulation, etc., is still topic of interest. An overview of recent advances in AP/HTPB

propellant pyrolysis and combustion from an experimental perspective is provided by Brill and Budenz (2000).

2. Components and properties

The choosing of propellant type is at the core of any solid rocket motor design. The desirable characteristics for a solid propellant are high specific impulse, predictable and reproducible burning rate and ignition characteristics, high density, ease of manufacturing, low cost, and good aging characteristics. In safety point of view propellants should produce low-smoke exhaust and not be prone to combustion instability. In addition, they should have adequate thermophysical and mechanical properties over the intended range of operating and storage conditions. Propellants are typically classified as homogeneous or heterogeneous, according to their chemical composition and physical structure. The former contain fuels and oxidizers, which are chemically linked at the molecular level. The latter include fuel and oxidizers, which are mixed physically. The ingredients of homogenous propellants belong to a wide spectrum of chemical families, but mostly fall into one of four categories: nitramines (RDX, HMX, HNIW also known as CL-20, HNF), azides (GAP, BAMO, AMMO), nitrate esters (NG, NC, BTTN, TMETN, DEGDN), or nitrates (ADN, AN). In composite propellants, the main ingredients often used are oxidizers such as AP, AN, and KN, and fuels such as HTPB, HTPE, and CTPB (Beckstead et al., 2007).

The material densities are typically in the range of 1.2 – 2.0 g cm^{-3} (Beckstead et al., 2007). The heat of formation varies widely and is instrumental in determining the flame temperature and the total energy released during combustion. Numbers of experimental diagnostics and analytical models have helped obtain reliable data for the thermal decomposition, thermophysical properties, and flame structures of these propellants. Different chemical ingredients present in a solid propellant and their functions are as follows.

2.1. Oxidizer

Oxidizers are principle ingredients, which produce the high energy on combustion. One of the most commonly used

oxidizers is AP. AP dominates the oxidizer list because of its good characteristics that include compatibility with other propellant ingredients, good performance, and availability. AN and KN are also used in some applications. Although the inorganic nitrates are relatively low-performance oxidizers compared to perchlorates, they are used because of low cost and smokeless and non-toxic exhaust (Chaturvedi and Dave, 2011, 2012; Meda et al., 2007).

2.2. Metal fuel

Metal fuels such as aluminum and boron are frequently added to propellant mixtures (Galfetti et al., 2003, 2004). Aluminum, one of the widely used metal additives, is used in the form of small spherical particles (5–60 µm) in a wide variety of solid propellants. Aluminum particles usually comprise 14–20% of the propellant weight. Addition of metal fuel enhances the heat of combustion, propellant density, combustion temperature, and hence the specific impulse. There are some compounds, which can act as both fuel and oxidizer such as NG and AP.

2.3. Binder

Binders provide structurally a matrix in which solid granular ingredients are held together in a composite propellant. The raw materials are liquid prepolymers or monomers. The binder impacts the mechanical and chemical properties, propellant processing and aging of the propellant. Binder materials typically act as a fuel, which gets oxidized in the combustion processes. Commonly used binders are HTPB, CTPB, and NC. Sometimes GAP is also used as energetic binder, which increases the energy density and performance of the propellant. HTPB has been abundantly used in the recent years, as it allows higher solid fractions (total 88–90% of AP and Al) and relatively good physical properties (Galfetti et al., 2006; Meda et al., 2005).

2.4. Modifier or Catalyst

A burning-rate catalyst helps increase or decrease the propellant burning rate. It is sometimes also referred to as burning-rate modifier. It can be used to modify the burning rate of specific grain design to a desired value. Substances such as iron oxide increase the burning rate, while lithium fluoride decreases the burning rate (Sutton and Biblarz, 2001). These materials help tailor the burning rate to fit the grain design and the thrust-time requirement.

Nowadays lots of work have been done on propellants by using various catalysts (Singh et al., 2008, 2009a,b,c, 2010, 2011, 2012; Chaturvedi and Dave, 2011a,b; Srivatava et al., 2010; Dubey et al., 2012). In recent researchers mainly focus on catalyst of nano size. Several experimental results show that catalytic activity of nano sized catalyst remarkably increased as compared to their bulk size. Complete thermal decomposition of AP occurs at much lower temperature. Burning rate of propellants also enhanced with nano sized catalyst.

2.5. Plasticizer

It is a relatively low-viscosity organic liquid, which also contributes to the thermal energy on oxidation. Addition of

plasticizer improves the processing properties of propellant remarkably. Some of the commonly used plasticizers are DOA, NG, GAP, and DEP.

2.6. Curing agent

A curing agent causes the prepolymers to form longer chains of larger molecular mass and interlocks between chains. Curing agents are also referred to as crosslinkers. They solidify and harden the binder. Although present in a minor amount, its presence impacts the propellant physical properties, manufacturability, and aging considerably. It is used only with composite propellants. HMDI, TDI, and IPDI are some examples of curing agents.

2.7. Additive

Other substances in minor quantities are often added to solid propellants. Opacifier is an additive to make the propellant more opaque to prevent radiative heating at places other than burning surface. Bonding agents improve the adhesion between the solid propellant and the motor case. Desensitizing agents are added to make the propellant resistant to accidental ignition from unwanted energy stimulus. Organic oxidizers, which are explosive organic compounds with – NO₂ radical or other oxidizing fractions, are also incorporated into the molecular structure (Sutton and Biblarz, 2001).

3. Classification

Mainly two types of solid propellants (homogeneous and heterogeneous) are distinguished by their constituent ingredients and the condition in which they are linked. In a homogeneous propellant, the ingredients are linked chemically and the resulting physical structure is homogeneous throughout. Typical examples of homogeneous propellants are single-base (NC and additives), double-base (NC, NG and additives), and triple-base (NC, NG, NQ, and additives) propellants. In a heterogeneous or composite propellant, the ingredients are physically mixed, leading to a heterogeneous physical structure. It is composed of crystalline particles acting as oxidizer and organic plastic fuels acting as binder to adhere oxidizer particles together. The ingredients often used as oxidizers are AP, AN, ADN, RDX, and HMX. The most commonly employed binders are either inert (typically HTPB, ballistic modifiers, and cross-linking agents) or active (NG and NC, polyether polymer, and azide polymer such as GAP, BAMO, and AMMO) (Kubota, 2002; Ramakrishna et al., 2002; Yang et al., 2000).

3.1. Homogeneous solid propellants

3.1.1. Single-base propellants

The main ingredient in a single-base propellant is NC, gelatinized with ethyl alcohol as solvent. NG is made by acid nitration of natural cellulose fibers from wood or cotton and is a mixture of several organic nitrates. Small amounts of chemical stabilizer and flame suppressant are also added. The propellant grain is coated with carbon black to keep the surface smooth (King, 1978).

3.1.2. Double-base propellants

Double-base propellants are one of the oldest propellants. They are known to have nearly smokeless exhaust. The main ingredients in double-base propellants are NC and an energetic nitrate ester such as NG, TMETN, or DEGDN. These nitrate esters are liquid at room temperature and are used to produce a plasticized gel network resulting in a homogenous physical structure. The physiochemical properties of double-base propellants such as energy density, mechanical properties, and combustion characteristics and stability depend on the proportions of NC, nitrate ester, stabilizers, plasticizers, and other catalysts. Two types of double-base propellants, extruded and cast, are distinguished by the manufacturing process. By adding crystalline nitramines the performance and density can be improved. This is sometimes called as cast-modified double-base propellant. Aluminum can be added to suppress combustion instability as well as improve specific impulse. Sometimes azides (GAP) are added to double-base propellants, which can act as a plasticizer. The energy density of the resultant propellant also increases (Liau and Yang, 1995).

3.1.3. Composite modified double base propellants

Composite modified double base (CMDB) propellants start with a nitrocellulose/nitroglycerin double base propellant as a binder and add solids (typically ammonium perchlorate and powdered aluminum) normally used in composite propellants. The ammonium perchlorate makes up the oxygen deficit introduced by using nitrocellulose, improving the overall specific impulse. The aluminum also improves specific impulse as well as combustion stability. High performing propellants such as NEPE-75 used in Trident II D-5 replace most of the AP with HMX, further increasing specific impulse. The mixing of composite and double base propellant ingredients has become so common as to blur the functional definition of double base propellants. The physical structure of CMDB is somewhat heterogeneous, and the physicochemical properties are intermediate between composite and homogeneous propellants (King, 1978).

3.1.4. Triple-base propellants

NQ can be added to a double-base propellant to form a triple base propellant. NQ contains a relatively high amount of hydrogen atoms within its molecular structure that lowers the average molecular weight of the propellant combustion products. If instead of NQ, crystalline AP, HMX, or RDX particles are can be used then the propellant is called as CMDB (King, 1978).

3.2. Heterogeneous solid propellants

Heterogeneous propellants are mixtures of crystalline oxidizer particles binded within a polymeric fuel matrix. The commonly used oxidizers such as AP and AN produce high oxygen concentrations on thermal decomposition. The fuel used is the hydrocarbon-based polymers such as HTPB, CTPB, and PBAN. Typically high concentrations of oxidizers are used to give high specific impulse. Aluminum particles are usually added to further increase the specific impulse (Cai et al., 2008; Jackson and Buckmaster, 2002; Knott and Brewster, 2000, 2002; Knott et al., 2001; Massa et al., 2005).

3.2.1. AP-composite propellants

AP-based composite propellants usually produce white smoke on combustion. This is because one of the combustion products HCl nucleates the condensation of moisture in the atmosphere, resulting in fog or mist. Such smoke is not produced if AN is used, but it lowers the performance due to reduction in the specific impulse. AP-HTPB is the most commonly used combination because HTPB is considered to be a superior binder to achieve high combustion performance as well as desired propellant physical and mechanical properties. Azide polymers such as GAP and BAMO are also used with AP or AN to formulate composite propellants. The addition of metal fuel such as Al allows a significant increase in the adiabatic flame temperatures of composite propellants. When aluminum is used, the combustion products contain a substantial amount of aluminum oxide (Al_2O_3) in the chamber, which is mostly present in the liquid phase.

3.2.2. Ammonium Nitrate based Propellants

One of the primary products of combustion of AP-based propellants is HCl, which in the presence of water forms hydrochloric acid, which produces smoke and is highly toxic. Realizing the significance of chlorine free propellants there have been many attempts have been made to develop clean burning propellants. Many of these attempts as can be seen are based on AN as the oxidizer. Ammonium Nitrate (AN) is one of the most appropriate oxidizer for propellant compositions that meet the above requirements. Though the experiments on AN as a high-performance oxidizer for SRB (space shuttle's solid rocket boosters) in place of AP are in their infancy, gas generator compositions have established its use as an efficient oxidizer. Both double-base and composite (without metal) propellants are used extensively with AN or as a mixture of AN and guanidine nitrate in gas generators (Chaturvedi and Dave, 2011a,b; Meda et al., 2007). AN composite propellants provide desired exhaust properties such as high nitrogen content, low water, modest amounts of solid particles, and a relatively nonhazardous exhaust. Further, AN propellant formulations are relatively insensitive to temperature and impact and have good strength properties over a wide range of temperature. AN-based systems have several positive features including clean burning and smokeless exhaust. They can be used as a substitution for AP. Though AN-based systems have several positive features such as clean burning and smokeless exhaust they are not free from drawbacks, and substitution of AP with AN for high-performance systems is not straightforward. The main problems associated with AN in its use as an oxidizer in propellants include the following: phase transformation around room temperature (32°C), which is accompanied by significant volume expansion that results in crack formation in the propellant grain; hygroscopicity; low burning rate; and low energy. Many attempts have been made to overcome these problems and to realize a better phase transition and combustion behavior for AN-based propellants (Chaturvedi and Dave, 2011a,b; Meda et al., 2007).

3.2.3. Nitramine composite propellants

These propellants contain crystalline nitramines such as RDX and HMX mixed with a polymeric binder. The polymeric binders are similar to the ones used in AP-based composite propellants. Nitramine composite propellants offer the advantage of

reduced infrared emissions due to the reduced CO_2 and H_2O concentration as compared to AP-HTPB propellants (Kubota, 2002).

3.2.4. Minimum-signature (smokeless) propellants

One of the most active areas of solid propellant research is the development of high-energy, minimum-signature propellant using CL-20 (China Lake compound #20), $\text{C}_6\text{H}_6\text{N}_6(\text{NO}_2)_6$, which has 14% higher energy per mass and 20% higher energy density than HMX. The new propellant has been successfully developed and tested in tactical rocket motors. The propellant is non-polluting; acid free, solid particulates free, and lead free. It is also smoke free and has only a faint shock diamond pattern that is visible in the otherwise transparent exhaust. Without the bright flame and dense smoke trail produced by the burning of aluminized propellants, these smokeless propellants eliminate the risk of giving away the positions from which the missiles are fired. The new CL-20 propellant is shock-insensitive (hazard class 1.3) as opposed to current HMX smokeless propellants which are highly detonable (hazard class 1.1). CL-20 is considered a major breakthrough in solid rocket propellant technology but has yet to see widespread use because costs remain high.

4. Combustion

Understanding the thermal decomposition and combustion characteristics of energetic materials is crucial before they are employed in actual rocket motors. The combustion characteristics of concern include pressure and temperature sensitivities of the burning rate, propellant surface condition, and spatial distribution of energy release, temperature, and species concentrations. Combustion of a solid propellant involves an array of intricate physiochemical processes evolving from the various ingredients that constitute the propellant. Thus it is important to study and characterize the burning properties of the specific ingredients that are used in solid propellants (Kubota, 2002; Ramakrishna et al., 2002; Yang et al., 2000; King, 1978; Liau and Yang, 1995; Cai et al., 2008).

Combustion wave structure of a composite propellant is much different and more complex than that of a homogeneous propellant. One of the main differences is the diffusion flame structure of a composite propellant versus the premixed flame structure of a homogeneous propellant (Beckstead et al., 2007).

The AP particles first decompose in the sub-surface region to form perchloric acid (HClO_4), and the HTPB binder decomposes to produce fuel in the form of hydrocarbon fragments and hydrogen. HClO_4 decomposes further to form smaller oxidizing species. These decomposed gases consisting of fuel and oxidizer components mix together to form a diffusion flame above the propellant-burning surface. The flame structure, however, is more complex as there are individual premixed monopropellant flames from AP and partially mixed flames from HTPB, in addition to the diffusion flame from their decomposition products. The luminous flame is attached to the burning surface and there is no dark zone as seen in double-base propellants. If aluminum particles are present in a composite propellant, they break loose from the surface and continue to react in the gas flow (Yang et al., 2000).

The combustion of AP/HTPB composite propellant involves an array of intricate physiochemical processes including the following: (1) conductive preheating, decomposition, and phase transition in the condensed phase; and (2) multi-stage reactions in the gas phase. Since the oxidizer and fuel binder are not linked chemically, the combustion characteristics of AP and HTPB are first examined separately in order to facilitate the construction of an integrated model for the overall propellant combustion.

4.1. Combustion of AP Monopropellant

Combustion of AP monopropellant has been extensively studied in the past (King, 1978). The AP crystal first experiences a phase transition from an orthorhombic structure to a cubic structure at 513 K. As the temperature increases, the crystal lattice becomes unstable and melts around 830 K. The dissociative sublimation and degradation of AP occurs at this temperature. The degradation results in a thin superficial reaction layer, approx. 70% consumption of the AP crystal. The remaining 30% undergoes a highly endothermic equilibrium dissociative sublimation ($\Delta H_{\text{dis}} = 58 \pm 2 \text{ kcal/mol}$) through a proton transfer producing gaseous ammonium and perchlorate acid. The species so generated subsequently undergo a sequence of chain reactions to form a premixed flame producing final products such as O_2 , NO , and N_2O , which act as major oxidizers in the gas phase reactions.

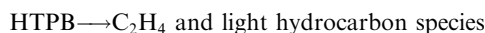
Based on the earlier reported literatures (Kuo and Summerfield, 1984; Guirao and Williams, 1971; Jacobs and Whitehead, 1969) a gas-phase reaction mechanism involved 14 species and 10 reactions to predict the temperature field and species concentrations. On the basis of this mechanism, Chu and Yang (1996) proposed a one-step kinetics model and predicted the flame temperature and major species concentrations of AP deflagration. Results indicate that the premixed flame is located very close to the propellant surface, with stand-off distances of about 9 and 1 mm at pressures of 20 and 70 atm, respectively. The flame height of AP monopropellant is about 1 to 2 orders of magnitude lower than that of the final diffusion flame in AP/HTPB composite propellant combustion.

4.2. Pyrolysis of HTPB Binder

HTPB is long-chain, cross-linked, and high molecular-weight polymer. Literature (Boldyrev, 2006) reported that the pyrolysis of HTPB is highly dependent on the heating rate. At low heating rates (less than 100 K/min), the pyrolysis is known to occur via a two-stage mechanism. The first stage involves endothermic depolymerization, forming monomer butadiene, cyclopentene, 1,3-cyclohexadiene, and 4-vinylcyclohexene as the main gaseous products. Thermogravimetric analysis (TGA) studies show a 10–15% weight loss during this stage. In the second stage, the remaining residue cyclizes, cross-links, and undergoes further degradation. At heating rates higher than 100 K/min, the first stage prevails, with depolymerization as the main degradation process (Beck, 1987; Chen and Brill, 1991). In rocket-motor environments, since HTPB is exposed to extreme temperatures (above 2000 K), pressures (20–100 atm), and heating rates (as high as 106 K/s), there is

very little time for exothermic crosslinking and cyclization to take place.

Therefore, depolymerization becomes the dominant process. Radhakrishnan and Rama and Radhakrishnan (1981) identified the final degradation products using a gas chromatography (GC) technique. At temperatures below 770 K, the main gaseous product is butadiene, whereas a whole range of products arises as the temperature increases. At 1170 K, butadiene accounts for only 1–2% of the products, and the primary product is ethylene. In light of the above findings, the thermal decomposition of HTPB in a rocket-motor environment is assumed to undergo the following pathway:



4.3. Combustion of AP/HTPB Propellant

Three main points should be considered for a typical AP/HTPB composite propellant. First, the mass loading of AP is much higher than that of HTPB. Second, AP monopropellant is highly reactive and can sustain exothermic reactions without the presence of any fuel binder. Third, the size of AP particles plays a decisive role in dictating the burning behavior of the composite propellant. Thus AP degradation is the main controlling factor in the modeling of condensed-phase processes. HTPB is assumed to influence the combustion only through the participation of its degradation products in the gas-phase reactions. Consequently, the condensed-phase modeling is conducted solely on AP, and the HTPB regression rate is determined by the overall energy balance. A primary diffusion flame can occur through the reactions between HTPB pyrolysis products and ammonia-derived oxidizer (HClO_4). This flame, however, may exist only at low pressures, due to the competing reaction effects. In rocket motors, the high chamber pressure renders rapid AP deflagration with an exceedingly low flame height. The ammonia-derived oxidizer can hardly meet HTPB pyrolysis species through the diffusion process, and is almost completely consumed in the AP primary flame. The effect of the primary diffusion flame can thus be neglected in a high-pressure environment. To facilitate modeling, the overall pyrolysis product of HTPB is assumed to be ethylene. The validity of this approach is further supported by the chemical equilibrium analyses reported earlier (Arisawa and Brill, 1996) of AP/HTPB and AP/ethylene.

The mass fraction of AP is 80% for both cases (AP/HTPB and AP/ethylene). Fairly good agreement is obtained for the equilibrium species concentration. The flame temperature, however, is over predicted by 100 K if HTPB is replaced by C_2H_4 , a phenomenon pointed to the endothermic depolymerization and pyrolysis of HTPB to form C_2H_4 . Both mixtures exhibit the highest flame temperature when the AP mass fraction reaches a stoichiometric value of 88%. The substitution of ethylene for the HTPB pyrolysis products in the current modeling of the gas-phase combustion appears to be reasonable.

5. Burning properties

The performance of a rocket motor depends mainly on the burning rate of the propellant (Gordon and McBride, 1994). At any instant, the burning rate governs the amount of gas generated in the combustion chamber and the mass flowing

out from the motor. The burning rate (r) is a function of many parameters such as propellant composition, chamber pressure, and initial grain temperature. It can also be influenced by phenomena such as erosive burning, radiative emissions, chamber pressurization rate, and combustion instability occurring inside the rocket motor (Gordon and McBride, 1994; Brewster and Mullen, 2011; Waeschel and Wenograd, 2000). For most propellants, it is possible to express r as an empirical function of chamber pressure given by

$$r = ap^n \quad (1)$$

where the burning rate is usually expressed in cm s^{-1} or in s^{-1} and the chamber pressure p is in MPa or psia. The constants a and n are called as the temperature coefficient and pressure exponent, respectively. The equation holds for all commonly used homogeneous and composite propellants. The constant a is not dimensionless and is influenced by the initial propellant grain temperature. The exponent n is influenced by the chamber pressure (Sutton and Biblarz, 2001). For minimum variation in the thrust or chamber pressure, the pressure exponent and the temperature coefficient should be small.

The propellant burning rate is also very sensitive to the initial grain temperature, which affects the propellant surface temperature and hence the rates of chemical reactions. Composite propellants exhibit a wide range of burning rates. For AP-based composite propellants, the burning rate strongly depends on the AP particle size. This is attributed to the diffusion flame structure that arises from the propellant surface. With a fixed AP content in a formulation, the burning rate increases with decreasing particle size.

The adiabatic flame temperature exhibited by the propellant is also an important property, as it directly influences the specific impulse. The flame temperature is highly dependent on the composition of the propellant. The burning rate of a solid propellant can increase during the motor operation on account of a phenomenon called erosive burning. It is caused by the high-velocity flow of hot combustion gases over the burning propellant surface. Such a high-velocity flow enhances turbulent mixing in the boundary layers and the heat transfer to the propellant, thereby increasing its burning rate. This can affect the motor performance significantly. While designing solid rocket motors, erosive burning should be either avoided or controlled to be reproducible from one motor to another so that the motor performance can be predicted accurately.

The radiative emissions and combustion instability occurring inside a solid rocket motor are some of the other factors that can influence the propellant burning rate significantly. The radiative emission from the hot combustion products to the propellant surface can increase the burning rate. Combustion instability caused either by acoustic waves or by vortex shedding can also affect the burning rate. The ensuing flow oscillations lead to substantial increase in heat-transfer rate, gas velocity, and pressure, which in turn affect the instantaneous burning rate.

6. Ignition

The ignition of a propellant grain in a rocket motor is caused by an igniter attached on the motor. The igniters are usually solid propellants that provide a rapid heat release and high

gas evolution. Extruded double-base propellants are often employed, usually as a large number of cylindrical pellets. One of the common igniter formulations uses 20–35% boron, 65–80% potassium nitrate with 1–5% of binder. Solid propellant ignition consists of a series of complex rapid events, which begin on receipt of a starting signal. This process include heat generation, transfer of heat from the igniter to the grain surface, spreading the flame over the entire burning surface, filling the chamber free volume with gas, and elevating the chamber pressure. The igniter generates the heat and gas required for motor ignition. During the ignition process, the heat generated from the igniter starts the burning of propellant grain. The flame spreads quickly until the complete grain is ignited. Then the chamber is completely filled with combustion products for reaching the operating pressure. The ignition process is usually completed within a fraction of a second (Gordon and McBride, 1994; Brewster and Mullen, 2011; Waeschel and Wenograd, 2000; Balzer et al., 2004).

7. Conclusion

A solid propellant contains several chemical ingredients such as oxidizer, fuel, binder, plasticizer, curing agent, stabilizer, and cross-linking agent. The specific chemical composition depends on the desired combustion characteristics. Different chemical ingredients and their proportions lead to different physical and mechanical properties, combustion characteristics, and performance. The propulsive performance of a solid propellant critically depends on its combustion characteristics including pressure and temperature sensitivities of the burning rate, and spatial distribution of energy release, temperature, and species concentrations. There is also scope for further research to improve the performance of propellants by use of nanosize catalyst. Nowadays it is the one of the main issues for the research.

Acknowledgments

The authors are grateful to Chemistry Department of KSKV University, Bhuj for laboratory facility. One of the authors Shalini Chaturvedi is also thankful to CSIR for Research associate (RA) fellowship.

References

- Arisawa, H., Brill, T.B., 1996. Flash pyrolysis of hydroxyl-terminated polybutadiene (HTPB) II: implications of the kinetics to combustion of organic polymers. *Combust. Flame* 106, 131–143.
- Balzer, J.E., Siviour, C.R., Walley, S.M., Proud, W.G., Field, J.E., 2004. Behaviour of ammonium perchlorate-based propellants and a polymer-bonded explosive under impact loading. *Proceedings A* 460, 781–806.
- Beck, W.H., 1987. Pyrolysis studies of polymeric materials used as binders in composite propellants: a review. *Combust. Flame* 70, 171–190.
- Beckstead, M.W., Puduppakkam, K., Thakre, P., Yang, V., 2007. Modeling of combustion and ignition of solid-propellant ingredients. *Prog. Energy Combust. Sci.* 33 (6), 497–551.
- Boldyrev, V.V., 2006. Thermal decomposition of Ammonium Perchlorate. *Thermochim. Acta* 443, 1.
- Brewster, M.Q., Mullen, J.C., 2011. Burning-rate behavior in aluminized wide-distribution AP composite propellants. *Combustion, Explosion, Shock Waves* 47 (2), 200–208.
- Brill, T.B., Budenz, B.T., 2000. Flash pyrolysis of ammonia perchloratehydroxylterminated-polybutadiene mixtures including selected additives. In: Yang, V., Brill, T.B., Ren, W.Z. (Eds.) *Solid Propellant Chemistry, Combustion and Motor Interior Ballistics*, Progress in Astronautics and Aeronautics, AIAA, NY, vol. 185, pp. 3–23.
- Cai, W.D., Thakre, P., Yang, V., 2008. Model of AP/HTPB composite propellant combustion in rocket motor environments. *Combust. Sci. Technol.* 180, 2143–2169.
- Chaturvedi, S., Dave, P.N., 2011a. Nano metal oxide: potential catalyst on thermal decomposition of ammonium perchlorate. *J. Exp. Nanosci.*, 1–27.
- Chaturvedi, S., Dave, P.N., 2011b. A Review on the Use of Nanometals as Catalysts for the Thermal Decomposition of Ammonium Perchlorate; J. of Saudia Chemical society, in press. doi: <http://dx.doi.org/10.1016/j.jscs.2011.05.009>.
- Chen, J.K., Brill, T.B., 1991. Chemistry and kinetics of hydroxyl-terminated polybutadiene (HTPB) and diisocyanate-HTPB polymers during slow decomposition and combustion-like conditions. *Combust. Flame* 87, 217–232.
- Chu, W., Yang, V., 1996. Combustion of AP-based composite propellant in a rocket motor flow environment. In: 32nd Joint Propulsion Conference, AIAA, pp. 96–2885.
- Dubey, R., Srivastava, P., Kapoor, I.P.S., Singh, G., 2012. Synthesis, characterization and catalytic behavior of Cu nanoparticles on the thermal decomposition of AP, HMX, NTO and composite solid propellants. *Thermochimica Acta* 549, 102–109.
- Galfetti, L., De Luca, L., Severini, F., Maggi, F., Marra, G., Meda, L., 2003. *Explosion Shock Waves* 41 (6), 680.
- Galfetti, L., Severini, F., DeLuca, L.T., Marra, G.L., Meda, L., Braglia, R., 2004. Ballistics and Combustion Residues of Aluminized Solid Rocket Propellants. In: *Proceedings of the 9-IWCP, Novel Energetic Materials and Applications*, vol. 18.
- Galfetti, L., De Luca, L.T., Marra, G., Meda, L., Severini, F., Cerri, S., Lentini, L., Babuk, V., 2006. Intl. Astronautical Congress IAC 2–6 Oct. 2006, Valencia, C4.3.03.
- Gordon, S., McBride, B.J., 1994. *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications*. NASA Reference Publication, 1311.
- Guirao, C., Williams, F.A., 1971. A model for aluminum perchlorate deflagration between 20 and 100 atm. *AIAA J.* 9 (7), 1345–1356.
- Jackson, T.L., Buckmaster, J., 2002. Heterogeneous propellant combustion. *AIAA J.* 40 (6), 1122–1130.
- Jacobs, P.W.M., Whitehead, H.M., 1969. Decomposition and combustion of ammonium perchlorate. *Chem. Rev.* 4, 551–590.
- King, M.K., 1978. Model for steady state combustion of unimodal composite solid propellants. *AIAA Paper*, 1978-216.
- Kishore, K., 1979. Comprehensive view of the combustion models of composite solid propellants. *AIAA J.* 17, 1216–1224.
- Knott, G.M., Brewster, M.Q., 2000. Two-dimensional combustion modeling of heterogeneous solid propellants with finite Peclet number. *Combust. Flame* 121, 91–106.
- Knott, G.M., Brewster, M.Q., 2002. Modeling the combustion of propellant sandwiches. *Combust. Sci. Technol.* 174, 61–90.
- Knott, G.M., Jackson, T.L., Buckmaster, J., 2001. Random packing of heterogeneous propellants. *AIAA J.* 39 (4), 678–686.
- Kubota, N., 2002. *Propellants and Explosives, Thermochemical Aspects of Combustion*. Wiley-VCH, Weinheim, Germany.
- Kuo, K.K., Summerfield, M. (Eds.), 1984. *Fundamentals of Solid Propellant Combustion*, Progress Astronautics and Aeronautics, vol. 90. AIAA, p. 891.
- Liau, Y.-C., Yang, V., 1995. Analysis of RDX monopropellant combustion with two-phase subsurface reactions. *J. Propul. Power* 11, 729–739.
- Massa, L., Jackson, T.L., Buckmaster, J., 2005. New kinetics for a model of heterogeneous propellant combustion. *J. Propul. Power* 21 (5), 914–924.

- Meda, L., Marra, G.L., Galfetti, L., Inchingalo, S., Severini, F., De Luca, L., 2005. *Compos. Sci. Technol.* 65 (5), 769.
- Meda, L., Marra, G., Galfetti, L., Severini, F., De Luca, L., 2007. Nano-aluminum as energetic material for rocket propellants. *Mater. Sci. Eng. C* 27, 1393–1396.
- Rao, Rama, M. Radhakrishnan, T.S., 1981. Thermal decomposition of polybutadienes by pyrolysis gas chromatography. *J. Polymer Sci.* 19 (12), 3197–3208.
- Ramakrishna, P.A., Paul, P.J., Mukunda, H.S., 2002. Sandwich propellant combustion: modeling and experimental comparison. *Proc. Combust. Instit.* 29, 2963–2973.
- Ramohalli, K.N.R., 1984. Steady-State burning of composite propellants under zero crossflow situation. In: Kuo, K.K., Summerfield, M. (Eds.), *Fundamentals of Solid-Propellant Combustion*, Progress in Astronautics and Aeronautics. AIAA, New York.
- Singh, G., Inder Pal Singh Kapoor, I.P.S., Shalini Dubey, S., Siril, P.F., JianHua, Yi, Feng Qi, ZHAO, Rong-Zu, HU, 2008. Effect of mixed ternary transition metal ferrites nanocrystallites on the thermal decomposition of ammonium perchlorates. *Thermochimica Acta* 477, 42–47.
- Singh, G., Kapoor, I.P.S., Dubey, S., 2009a. Bimetallic nanoalloys-Preparation, characterization and catalytic activity. *J. Alloys Compd.* 480, 270–274.
- Singh, G., Kapoor, I.P.S., Dubey, S., Siril, P.F., 2009b. Kinetics of thermal decomposition of ammonium perchlorate with nanocrystals of binary transition metal ferrites. *Prop. Explo. Pyro.* 34, 72–77.
- Singh, G., Kapoor, I.P.S., Dubey, S., Siril, P.F., 2009c. Preparation, characterization and catalytic activity transition metal oxide nanocrystals. *J. Sci. Conf. Proce.* 1, 11–17.
- Singh, G., Kapoor, I.P.S., Dubey, R., Srivatava, P., 2010. Preparation, characterization and catalytic behavior of CdFe₂O₄ and Cd nanocrystals on AP. *HTPB Compos. Solid Propellants* 511 (1–2), 112–118.
- Singh, G., Kapoor, I.P.S., Dubey, S., 2011. Nanocobaltite: preparation, characterization and their catalytic activity. *Prop. Explo. Pyro* 36, 367–372.
- Singh, G., sengupta, S.K., Kapoor, I.P.S., Dubey, S., Dubey, R., Singh, S., 2012. Nanoparticles of transition metals as accelerants in the thermal decomposition of ammonium perchlorate. *J. Energetic Mater.* <http://dx.doi.org/10.1080/07370652.2012.65618>.
- Srivatava, P., Dubey, R., Kapoor, I.P.S., Singh, G., 2010. Synthesis, characterization and catalytic effect of Bimetallic nanocrystal on the thermal decomposition of Ammonium perchlorate. *Indian J. Chem.* 49 (A), 1339–1344.
- Sutton, G.P., Biblarz, O., 2001. *Rocket Propulsion Elements*, seventh ed. John Wiley and Sons Inc..
- WaescheI, R.H.W., Wenograd, J., 2000. Calculation of solid-propellant burning rates from condensed-phase decomposition kinetics. *Combustion, Explosion, Shock Waves* 36, 1.
- Yang, V., Brill, T., Ren, W.Z. (Eds), 2000, *Solid-Propellant Chemistry, Combustion, and Motor Interior Ballistics*, Progress Astronautics and Aeronautics, vol. 185, AIAA, 990 p.