CHAPTER 6

The Propulsive Facet of High Energy Materials—II (Rocket Propellants)

6.1. Introduction to Rocketry

The Chinese are credited to have invented rockets several centuries back. Gunpowder-filled paper tubes sealed at one end with a wick on the other were known to propel themselves on ignition, soaring toward the sky against gravity. What started as a part of firework display in the early stages found its application in modern missiles and space missions during the last century. Today, the load carried by a rocket (commonly known as the "payload") can be either a warhead—conventional or nuclear—or a satellite that needs to be "injected" into a particular orbit of the Earth for communication purposes. Thus, rockets have become part and parcel of modern life for various applications such as entertainment or war or space research. Although long-range missiles with nuclear warheads threaten the very existence of mankind today, global space research programs hold great promise for advancement in various fields such as communication, weather prediction, and tapping the resources from Earth. When the famous U.S. astronaut Neil Armstrong created history by becoming the first human to set foot on the lunar soil on July 21, 1969 ("A small step for me but a giant leap for mankind"), his ecstasy and excitement were shared by several millions on Earth. Thus, the field of rocketry has become an inalienable part of today's science and technology. The aim of this chapter is just to introduce the basic principles of rocket propulsion and the role played by high-energy materials (HEMs) in the form of rocket propellants toward propulsion performance.

6.2 Basic Principles of Rocket Propulsion

A rocket motor basically consists of two parts: a propellant combustion chamber and a nozzle (see Figure 6.1). The chamber is a metallic tube sealed at one end and the rocket propellant (in the case of solid rocket propellants) is loaded through the open end. The propellant grain may be of varying shapes and sizes depending on the type of performance expected from the rocket. For example, it can be a solid cylinder or a tubular propellant grain, as shown in Figure 6.1. The annular space in the tubular propellant grain is called the "port." The loaded rocket chamber is then screwed onto a nozzle, which in most of cases is a convergent-divergent (CD) nozzle, as shown in Figure 6.1. An igniter placed in

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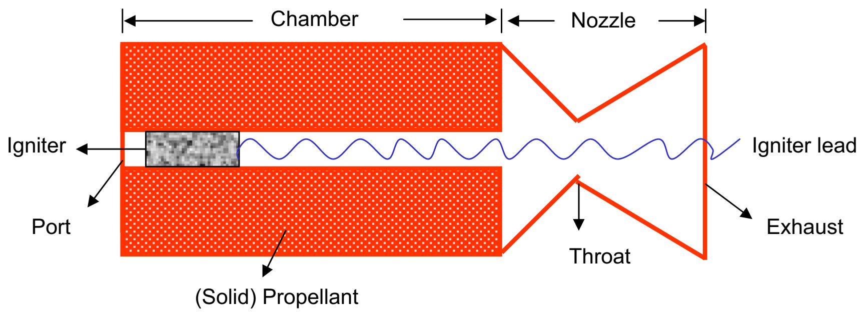


Figure 6.1
A Rocket Motor.

the port of the motor initiates the ignition of the entire propellant surface. This results in the production of high-temperature and high-pressure gaseous products, which get accelerated to very high velocities with the help of the nozzle. There is a tremendous increase in the velocity of the gaseous products when they expand from the "throat" portion of the nozzle to its exit. It is a matter of common knowledge that the exiting gases "kick back" the rocket as per Newton's Third Law of Motion, thereby resulting in propulsion.

The total thrust (F) with which a rocket is propelled has two components (Figure 6.2).

The first component of F is due to the thrust (F_1) created due to the imbalance of chamber pressure (P_c) and exhaust gas pressure (P_e) acting on the throat, the area of which is A_t. Therefore, it can be written,

$$F_1 = (P_c - P_e)A_t \tag{6.1}$$

(Note: Because the high-pressure gases are expanding after passing through the throat, P_c is always much greater than P_e; therefore, F_1 always has a positive value.)

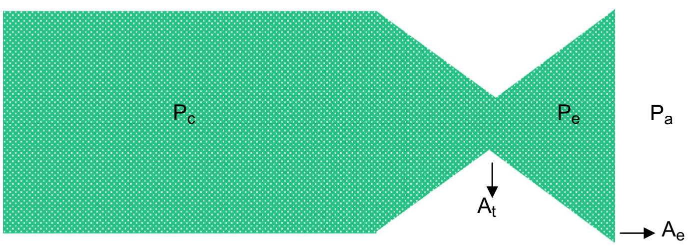


Figure 6.2
Components of Rocket Thrust.

The second component of F is due to the thrust (F_2) created due to the imbalance of exhaust gas pressure (P_e) and the ambient pressure outside of the rocket (P_a) acting on the exhaust, the area of which is A_e. Therefore, we can write

$$F_2 = (P_e - P_a)A_e \tag{6.2}$$

(Note: P_e is often greater than P_a (called the "underexpanded nozzle") so that F_2 also has a positive value. At times, the rocket is designed in such a way that $P_e = P_a$, resulting in $F_2 = 0$ (called the "optimum expanded nozzle").

There is also a possibility that $P_e < P_a$, as it happens when the nozzle becomes longer (resulting in an "overexpanded nozzle"), thereby resulting in negative values of F_2. P_a is not just the atmospheric pressure but the ambient outside pressure. For instance, when the rocket sails through vacuum in the interplanetary space, P_a is almost equal to zero and F_2 assumes the maximum value. The net propulsive force (F) a rocket experiences is the sum of F_1 and F_2; that is,

$$F = (P_c - P_e)A_t + (P_e - P_a)A_e \tag{6.3}$$

6.2.1 Types of Rocket Engines

A rocket is basically an energy conversion system converting the stored chemical energy in a propellant to the kinetic energy of the exhaust gases through nozzle expansion. One of the methods of classification of rocket engines is based on the physical status of the propellant. They are basically classified as

1. Solid propellant rockets,
2. Liquid propellant rockets, and
3. Hybrid propellant rockets.

The simplest rocket engine in the design and working point of view is a solid propellant engine, and most of this chapter describes solid propellant-based rockets. The solid propellant mostly consists of a mixture of an inorganic oxidizer (most commonly ammonium perchlorate (AP)) and a metallic fuel (e.g., aluminum) embedded in a matrix of polymer, which performs the dual functions of a binder (giving structural integrity of propellant grain) and fuel. Such a propellant is called a "composite propellant." For certain military applications, double-base rocket propellants (DBRPs) based on nitrocellulose (NC) and nitroglycerine (NG) are still being used.

As the name implies, the liquid propellant engine consists of a propellant that is a liquid. Again, there are two types of liquid propellant systems. The first is called a "monopropellant," in which the liquid is a single compound, the molecule of which has the fuel and oxidizer components. For example, nitromethane is a monopropellant

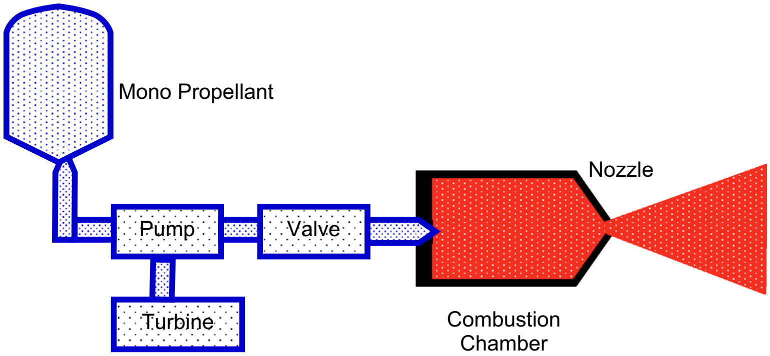


Figure 6.3
Schematic Representation of a Liquid Monopropellant Rocket Engine.

containing the fuel elements (carbon and hydrogen) and oxygen as the oxidizer. In any liquid rocket engines, the liquid propellant must be stored separately in a tank and needs to be pumped into the combustion chamber for operation. Figure 6.3 gives a schematic representation of a liquid monopropellant engine.

The second type of liquid rocket engine is based on a bipropellant system in which the oxidizer (in liquid form) and fuel (in liquid form) are separately stored in tanks. The oxidizer and fuel are pumped as per the required ratio into the rocket chamber for operation (Figure 6.4). This system obviously has more moving parts because of two separate flow systems; therefore, it has its own problems. Some of the well-known examples of bipropellant systems are as follows:

Oxidizer: Red fuming nitric acid (RFNA), hydrogen peroxide, and liquid oxygen
Fuel: Aromatic amines.

When we compare a solid propellant engine with a liquid propellant one, each has its advantages and disadvantages. For example, the design of a solid propellant grain is simpler and it does not have any additional moving parts (e.g., turbine/valve, etc.). However, once the solid propellant is ignited, it is difficult to stop or control the combustion whereas the flow of liquid oxidizer/fuel can be controlled.

In space programs and in advanced long-range ballistic missiles, the liquid propellant system is used either alone or along with a solid propellant system in different stages depending on the mission requirements.

The third type of rocket engine is called the "hybrid type" because it combines a solid (fuel/oxidizer) and a liquid (oxidizer/fuel). It is schematically shown in Figure 6.5. The liquid part (oxidizer; e.g., RFNA) is pumped into the rocket chamber containing the solid fuel (e.g., a polyurethane polymer). The hybrid propellant system has its own advantages and disadvantages of solid and liquid propellant systems.

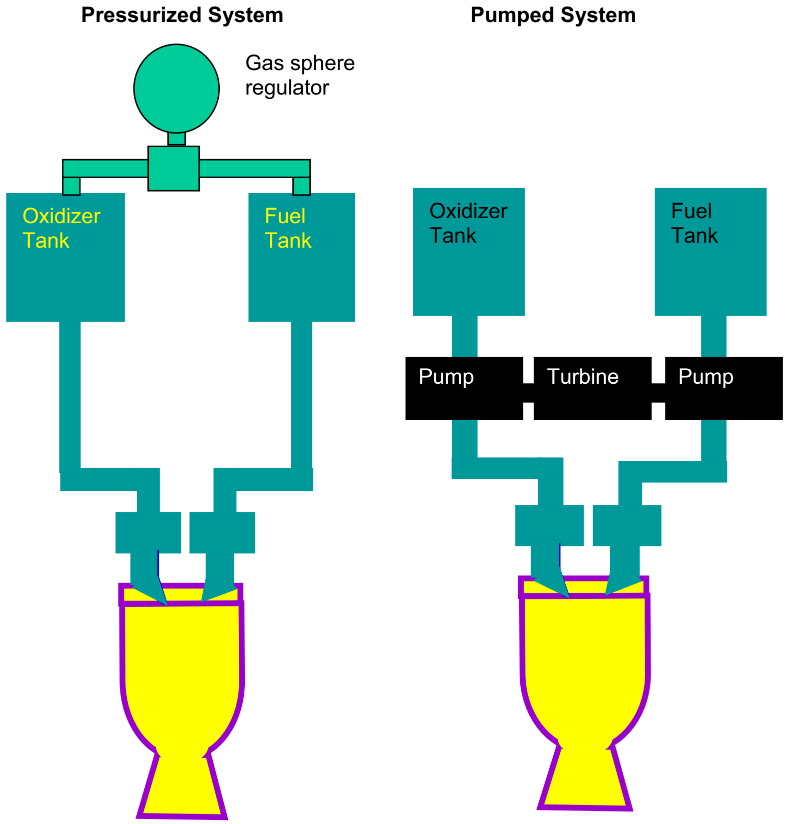


Figure 6.4
Schematic Representation of a Bipropellant Rocket Engine.

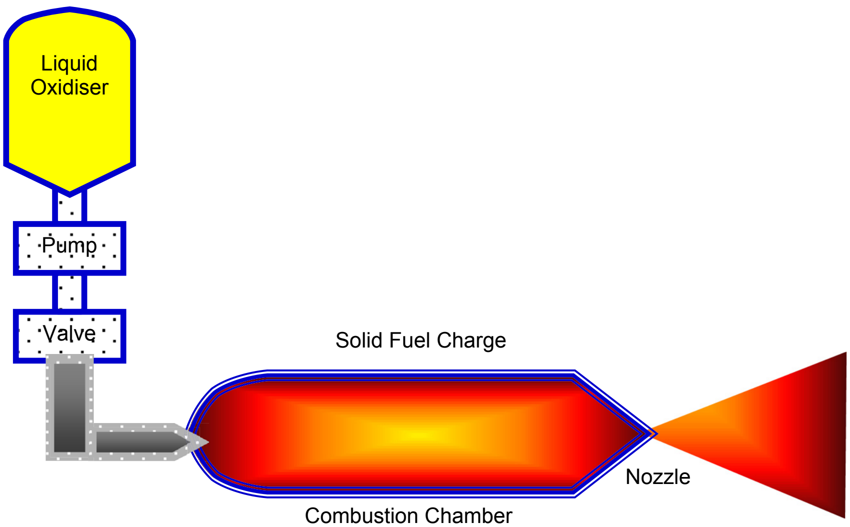


Figure 6.5
Schematic Representation of a Hybrid Liquid–Solid Rocket Engine.

6.3 Specific Impulse

Rocket designers have always been striving to achieve one goal—namely, to design a rocket

1. That can carry heavier payloads,
2. That can have longer ranges, and
3. In which the propellant consumption is minimal (analogous to fuel efficiency in automobiles).

Factors 1 and 2 demand that the total impulse developed by the rocket is quite high. Total impulse (I) is defined as $I = F \times t$ where F is the thrust developed by the rocket acting for a duration of time (t). In others words, factors 1 and 2 are directly proportional to $F \times t$. For complying with factor 3, the weight of the propellant consumed during the rocket flight (w) should be as little as possible. The term that considers these factors together to express the overall efficiency of a rocket propulsion system is called the "specific impulse" denoted by I_{sp}.

I_{sp} is accordingly expressed as

$$I_{sp} = \frac{F \times t}{w} \tag{6.4a}$$

This expression can also be written as

$$I_{sp} = \frac{\int F dt}{w} \tag{6.4b}$$

(or)

$$I_{sp} = \frac{F}{\dot{w}} \tag{6.4c}$$

where, $\dot{w}$ is the rate of consumption of propellant, being equal to $\frac{dw}{dt}$.

6.3.1 The Unit of I_{sp}

From Eqn (6.4a), we can see that F (i.e., thrust) and w (i.e., weight) have the same units—kilogram·meters per second squared (kg m s^{-2}; using SI units). Because they cancel out, only t remains. Therefore, specific impulse has the unit of seconds. For example, we can say that a given a propellant has an I_{sp} of 240 s.

6.3.2 I_{sp} and Exhaust Velocity of Gases

Let us consider a rocket cruising at a uniform velocity, and let the rocket function under the optimum nozzle expansion condition so that the second term in Eqn (6.3) is reduced to zero. If the exhaust gas velocity of the gases is v and the rate of loss of weight of the propellant (due to propellant burning) is $\dot{w}$, then the thrust (F) of the rocket, according to Newton's Second Law of Motion, is equal to the rate of change of momentum, which can be expressed as

$$F = \frac{d}{dt}(mv) = m\frac{dv}{dt} + v\frac{dm}{dt} = m\dot{v} + v\dot{m}$$

Because the rocket is moving with uniform velocity (i.e., $\dot{v} = 0$), in this case

$$F = \dot{m}v = \frac{\dot{w}v}{g} \tag{6.5}$$

(Because $m = w/g$).

Substituting this in Eqn (6.4c),

$$I_{sp} = \frac{\dot{w}v}{g} \times \frac{1}{\dot{w}} = \frac{v}{g}$$

$$I_{sp} = \frac{v}{g} \tag{6.6}$$

Therefore, I_{sp} is directly proportional to the exhaust velocity of gases (v).

Therefore, it is obvious that a propulsion scientist always endeavors to design his rocket—the hardware and the propellant—to achieve the highest possible value for the exhaust velocity (v).

Worked Example 6.1

A rocket develops a thrust of 10 tons by consuming 200 kg of propellant in 5 s. Calculate the specific impulse of the propellant used.

$$\text{The rate of propellant consumption} = \frac{200\text{ kg}}{5\text{ s}}$$

$$\dot{w} = 40\text{ kg s}^{-1}$$

$$I_{sp} = \frac{F}{\dot{w}} = \frac{10{,}000\text{ kg}}{40\text{ kg s}^{-1}} = 250\text{ s}$$

Why are we so specific about specific impulse?

It can be shown that the range of a rocket depends on the achievable *terminal velocity* (velocity of the rocket when the last gram of the propellant gets burnt), which again heavily depends on the I_{sp} of the propellant. I_{sp} plays a very vital role in the success of a mission. Every second gained in I_{sp} means very large gain in the range of a rocket. For instance, in the context of intercontinental ballistic missiles, an increase in the I_{sp} values by 1% and 5% increase their range by 7% and 45%, respectively. When a rocket is launched, its terminal velocity is severely limited because of two other forces: gravity and aerodynamic drag.

6.4 Thermochemistry of Rocket Propulsion

In the parlance of thermodynamics, a rocket can be called a "heat engine." The heat source is the high-temperature gaseous products obtained by the burning of the propellant. It uses part of that heat for the self-propulsive (or "useful") work, with the rest being wasted as heat loss by hot exhaust gases and by conduction of heat through walls of the rocket chamber. Therefore, rocket propulsion is the case of conversion of (a part of) the thermochemical energy of the propellant into the kinetic energy of the exhaust gases, a fact that is ultimately responsible for the rocket propulsion.

Let us designate that the initial heat content, pressure, volume, and temperature of the evolved gases during propellant deflagration be H_1, P_1, V_1, and T_1, respectively (Figure 6.6). The respective values for the exhaust gases can be assumed as H_2, P_2, V_2, and T_2. The change in heat content, $H_1 - H_2$, has been used to accelerate the exhaust gases to velocity v (i.e., assuming 100% conversion of thermal energy into kinetic energy of the exhaust gases). It can be written as

$H_1 - H_2 = \frac{1}{2}\frac{mv^2}{J}$ (i.e., kinetic energy of the gases)

(J = Joules constant = 4.18 J cal^{-1})

$$H_1 - H_2 = \frac{1}{2}\,\frac{w}{g}\,\frac{v^2}{J}$$

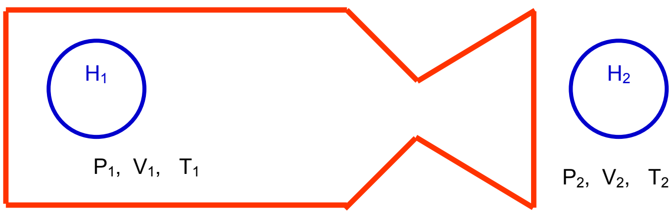


Figure 6.6
Change of Enthalpy and Other Parameters in Rocket Propulsion.

$$v = \sqrt{\frac{2gJ(H_1 - H_2)}{w}} \tag{6.7}$$

Assuming that the entire process is completely adiabatic (i.e., no heat is allowed to enter or leave the rocket motor system), it can be shown that

$$I_{sp} = \sqrt{\frac{2RT}{\overline{M}g}\left(\frac{\gamma}{\gamma-1}\right)\left[1-\left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}\right]} \tag{6.8}$$

where $\overline{M}$ = the average molecular weight of the exhaust gases, T = the flame temperature of the propellant, P_e = the pressure of the exhaust gases, P_c = the chamber pressure, γ = the ratio of specific heats of the gases (average value), and R = is the universal gas constant.

For a given set of values for P_e and P_c, assuming that the value of γ has only a limited influence, it is seen that the I_{sp} of a rocket propellant mainly depends on the adiabatic flame temperature of the propellant and the average molecular weight of the exhaust gas products. The higher values of T and lower values of $\overline{M}$ favor higher I_{sp} values. Equation (6.8) can be written in a simplified manner as

$$I_{sp} \,\alpha\, \sqrt{\frac{RT}{\overline{M}}} \tag{6.9}$$

As mentioned earlier, the average molecular weight of exhaust gases and the flame temperature (isochoric in the case of gun propellants and isobaric for rocket propellants) of propellants greatly influence their performance. Although in the case of gun propellants their performance parameter, the force constant, is directly proportional to nRT_v, the performance parameter of a rocket propellant, I_{sp}, varies in direct proportion to the square root of nRT_p. (Note: $n = 1/\overline{M}$.) The theoretical I_{sp} calculated for a given propellant (as calculated in the above worked example) does not exactly agree with the I_{sp} measured when the a rocket is fired. It is because, in theory, we assume the performance of the rocket under ideal conditions, which deviate from the actual conditions of performance, is as follows:

1. The high-pressure gases inside of the rocket motor do not completely obey ideal gas laws.
2. The rocket motor does not ensure 100% thermal insulation, and the perfect adiabaticity of performance cannot be assumed.
3. The composition/homogeneity of the gases is not uniform through the entire length of flow.
4. The chemical equilibrium gets continuously shifted throughout the flow.
5. There are losses due to multidimensional flow. (In an ideal rocket, the flow is in one dimension only; i.e., along the x-axis.)

6. There is heat loss due to friction and other dissipative factors.

Because of these deviations, the *delivered* I_{sp} of a rocket is always less than the theoretical I_{sp}.

6.5 Some Vital Parameters in the Internal Ballistics of Rockets

It is proposed to highlight the importance of some parameters that greatly influence the rocket performance.

6.5.1 Linear Burning Rate

The linear burning rate (LBR; r) of a solid propellant grain decides the value of the mass burning rate, which is sometimes referred to as the "mass flow rate" ($\dot{m}$). You may recall we have related these two parameters as

$$\dot{m} = rA\rho,$$

where A and ρ refer to the surface area exposed for burning and the density of the propellant, respectively.

The parameters r and $\dot{m}$ greatly affect the performance time of the rocket, the pressure build-up pattern in the rocket chamber, etc. In the case of a solid rocket propellant grain, the value of r depends on the factors presented in the following subsections.

6.5.1.1 Chamber Pressure

In the case of DBRPs (based on NC and NG), r and the pressure chamber (P_c) are related as

$$r = bP_c^n \tag{6.10}$$

This equation is known as Vielle's law, in which n is the pressure exponent and b is the burning rate coefficient. It takes the logarithmic form as (see Figure 6.7)

$$\log r = \log b + n \log P_c \tag{6.11}$$

At a given temperature, a plot of log r against log P_c yields a straight line, the slope of which yields the value of n. This is an empirical law, generally obeyed by double-base propellants mostly in the range of conventional operating pressures (from 20 to 100 kg cm^{-2}). Composite propellants (i.e., propellants containing a polymeric fuel cum binder containing uniform dispersion of an oxidizer such as AP and metallic fuel such as aluminum powder) do not obey this law. Although a perfect model for composite propellant burning has not been developed so far, Summerfield's model

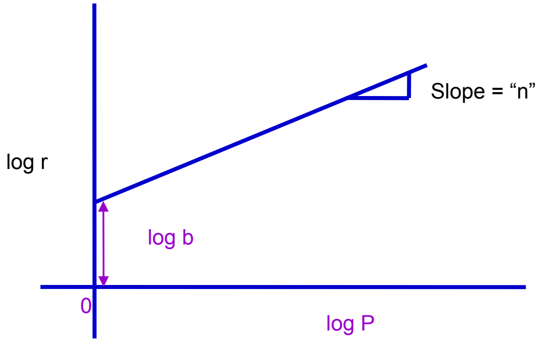


Figure 6.7
Plot of log r against log P for a Typical Double-Base Rocket Propellant.

has resulted in the following equation for composite propellants, which works reasonably well:

$$\frac{P}{r} = a + bP^{2/3} \tag{6.12}$$

with a and b being constants.

6.5.1.2 Temperature

The value of r increases with temperature. If r_1 and r_2 are the LBR values of a propellant at T_1 (in K) and T_2 (in K), respectively ($T_2 > T_1$), then the temperature sensitivity of burning rate at constant pressure, denoted as $(\pi_r)_P$, is given as

$$(\pi_r)_P = \frac{(\log r_2 - \log r_1)}{(T_2 - T_1)} \times 100$$

A rocket propellant designer always strives to keep the values of n and $(\pi_r)_P$ as low as possible. The higher these values, the greater are the chances for a catastrophic pressure build-up in a rocket motor.

6.5.1.3 Propellant Formulation

We have seen in the earlier chapters that if we formulate a propellant composition with high calorimetric value, then it results in higher flame temperature. It is natural to expect that in such cases, the heat transfer from the flame zone to the propellant surface will be faster, thereby increasing the r value of the propellant. In the case of composite propellants, apart from the aspects of the energetics of ingredients, the average particle size of the ingredients (oxidizer and metallic fuel) greatly affects the value of r for the same composition. The finer the particles, the greater is the value of r and vice versa.

The addition of burn rate catalysts also increases the value of r. For example, addition of salts/oxides of transition metals, such as Fe_2O_3 or $CuO \cdot Cr_2O_3$, as fine powder enhances the value of r. It is believed that electrons in the half-filled d orbitals of these transition metal atoms accelerate the decomposition of the AP (oxidizer) used in the composite propellants.

6.5.1.4 Erosive Burning

When high-velocity gases from the propellant erode the propellant surface, it results in faster heat transfer between the gas phase and solid phase, thereby increasing the value of r.

6.5.2 Characteristic Velocity

Referring back to the schematic representation of a rocket in Figure 6.1, let us ask: "What are the roles of propellants and the rocket nozzle in the rocket performance?" The first compartment (i.e., the chamber) ensures that the propellant burns as per the designed pressure-time profile and the high-pressure, high-temperature gases are ready to get into the nozzle to manifest their power. The total thermochemical energy of the propellant is being transformed into a high potential system ready for expansion through the nozzle. This thermochemical output is represented by the term "characteristic velocity" (C^*; pronounced as "see star"), which represents the thermochemical potential of the propellant.

The nozzle then takes over. The high-pressure gases are initially compressed through the convergent portion of the nozzle and then expanded with enormous power through its divergent portion. The efficiency of nozzle expansion, which determines the value of the exhaust velocity of gases, is called the "thrust coefficient" (C_F), which is basically a thrust amplification factor. C^* is characteristic of a propellant in combination with the chamber and is independent of nozzle design. On the other hand, C_F is a thrust amplification factor and depends on the nozzle design. C_F is given by the equation

$$C_F = \frac{F}{P_C A_t} \tag{6.13}$$

The numerator in the right-hand term of the equation refers to the realized thrust whereas the denominator refers to the thrust experienced *at the throat* before it is amplified by the divergent section of the nozzle. Because the exhaust velocity (v) is determined by C^* and C_F, it can be written

$$v = C^* C_F \tag{6.14}$$

Therefore, C^* can be defined as the exhaust velocity of the gases when their pressure does not undergo any amplification by the nozzle ($C_F = 1$). However,

$$I_{sp} = \frac{v}{g} \quad \text{from Eqn (6.6)}$$

$$\text{Therefore,} \quad I_{sp} = \frac{C^* C_F}{g} \tag{6.15}$$

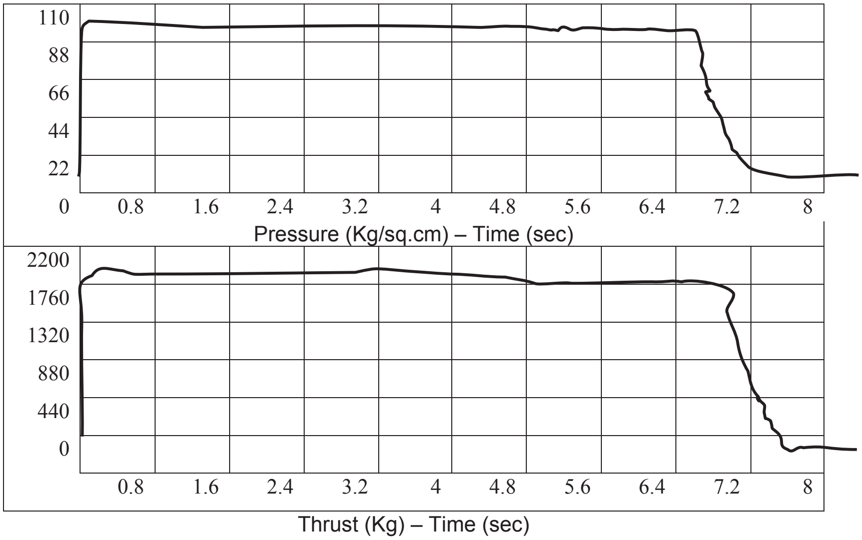


Figure 6.8
A Typical P—t and F—t Profile Obtained in a Static Rocket Firing.

$$I_{sp} = \frac{F}{\dot{w}} \quad \text{from Eqn (6.4c)}$$

$$\text{From Eqn (6.13),} \quad I_{sp} = \frac{C_F P_c A_t}{\dot{w}} \tag{6.16}$$

$$\text{From Eqns (6.15) and (6.16),} \quad C^* = \frac{g P_c A_t}{\dot{w}} \tag{6.17}$$

or

$$C^* = \frac{g A_t \int P dt}{W} \tag{6.18}$$

Using Eqn (6.18), C^* can be experimentally determined by finding out the area in a pressure—time curve (i.e., $\int Pdt$) by statically firing a rocket, knowing the values of W (weight of the propellant) and A_t (the cross-sectional area of the throat). A typical P—t and F—t profile curve obtained in a static rocket firing is shown in Figure 6.8. The areas under the P—t and F—t curves are obtained with great accuracy to calculate the parameters such as I_{sp} and C^*.

6.6. Design of a Rocket Propellant Grain

Depending on the requirements of a mission, such as payload, range, time of travel, etc., the ballistician finalizes certain basic parameters of propulsion such as (1) the total thrust needed, (2) the weight of the propellant (1 and 2 decide the I_{sp} of the propellant), (3) the action time (i.e., propellant burning time), (4) the density of the propellant, (5) the pressure index of the propellant, (6) the pressure at which the propellant should burn, (7) the A_e/A_t ratio, etc. Considering the mission requirements and the interdependence of many ballistic parameters, the ballistician has only a narrow choice. Once they finalize these, they turn to the propellant chemist and demand that the propellant must have characteristics such as

- An I_{sp} of x seconds,
- A C^* of y ms^{-1},
- An LBR of z mm s^{-1} at P kg cm^{-2},
- A pressure index in the range of n_1 and n_2,
- A density of ρ g cm^{-3}, etc.

It is now for the propellant chemist to use their expertise to formulate a composition that meets the demands of the ballistician. This is easier said than done. When they achieve one parameter (e.g., I_{sp}), some other parameters may start slipping away. For example, some of the higher energy (I_{sp}) versions of the solid rocket propellants may meet the demands of I_{sp} and C^* but may miserably fail in the requirement of pressure index. Or, they theoretically may feel confident about a particular formulation, but when they go to the process plant, they discover to their dismay that the composition is just not processable because the polymeric binder is too viscous to take the required solid loading of oxidizer and metallic fuel. It is like walking over a tight rope before the propellant chemist zeroes onto a certain formulation that satisfies the demands of the ballistician.

It is very often possible that the propellant chemist may not meet the demands of the ballistician exactly and there are slight variations. The ballistician then fine-tunes their design. Let us consider an example of a sustainer-type rocket propellant that burns from one end similar to a cigarette. The propellant chemist has finalized what they can offer and the ballistician works out the following parameters in sequence: (1) mass of the propellant, (2) the average burning surface, (3) the diameter of the grain, (4) the length of the grain, (5) the ratio of the burning area of the propellant at a given time to the area of the throat of the nozzle (called the K_N ratio), (6) the throat area (A_t), (7) the throat diameter, and (8) the area of the exit portion of the nozzle (A_e) on the basis of the A_e/A_t requirement.

Worked Example 6.2

How will you design a grain (cigarette-burning mode) of a rocket propellant considering the following requirements? (1) $I_{sp} = 200$ s, (2) $r = 0.5$ in s^{-1} at 1500 psi (which is the operating pressure), (3) $K_N = 400$ at 1500 psi, (4) density of the propellant = 0.05 lb in^{-3}, (5) $A_e/A_t = 10$, (6) thrust required = 1000 lb, and (7) burning time required = 20 s.

The sequence of calculation proceeds as follows:

1. Propellant weight : $\frac{F \times t_b}{I_{sp}} = \frac{1000 \times 20}{200} = 100$ lb
2. Grain length : $l = (r \times t_b) = 0.5 \times 20 = 10$ in
3. Grain volume : $\frac{\text{Weight}}{\text{Density}} = \frac{100}{0.05} = 2000\ \text{in}^3$
4. Propellant diameter (D) : Volume $= \left[\frac{\pi D^2 l}{4}\right]$, Substituting the value for volume and length, $D = 16$ in
5. Propellant burning area : $A_b = \frac{\pi D^2}{4} = 200\ \text{in}^2$

   (Cigarette-burning mode)
6. Area of the throat (A_t)

   Since $\text{K}_\text{N} = \frac{A_b}{A_t} = 400, \quad A_t = \frac{A_b}{400} = \frac{200}{400} = 0.5\ \text{in}^2$
7. Area of the exit (A_e)

$$\text{Since } \frac{A_e}{A_t} \text{ should be } 10, \quad \frac{A_e}{0.5} = 10, \quad A_e = 5\ \text{in}^2$$

The above seven parameters are calculated by the ballistician so that they can accordingly design and fabricate the rocket motor to realize their requirements using the above propellant. This is probably the simplest example that can be given to make beginners understand the methodology of grain design. In actual practice, it is far more complicated, particularly while dealing with large grains with complex internal configurations. The propellant design might need modification by considering factors such as the extent of erosive burning, combustion instability, compatibility with the ignition system, etc.

6.7. Chemistry of Solid Rocket Propellants

6.7.1. Choices and Limitations

As already mentioned, the job of a propellant chemist is unenviable. They get the requirement from the ballistician, and then their rope walking commences. The chemist has to take into account several factors that the propellant should satisfy, and the major ones are presented in the following subsections.

6.7.1.1 The Energetics

It is precisely the specific impulse (I_{sp}), the index of energy of any rocket propellant, that needs major consideration. I_{sp} varies depending on the nature of propellant. We have seen (Eqn (6.8)) that for a given chamber and exit pressure, I_{sp} mainly depends on the flame temperature and the average molecular weight of the products. We have seen in detail in Chapter 2 that the flame temperature depends on the calorimetric value (heat of explosion)

Table 6.1: Rocket propellant formulations with calorimetric value and theoretical I_{sp} values (values of P_c and P_e taken as 70 and 1 kg cm^{-2}, respectively).

Composition	Calorimetric Value (cal g^{-1})	I_{sp} (Theoretical; s)
Cast double base	800–1000	200–220
Extruded double base	800–1050	200–220
Composite	1000–1200	Up to 245
CMDB	900–1300	Up to 260
Nitramine double base	1000–1200	Up to 235

CMDB, composite modified double-base.

of the propellant whereas the average molecular weight ($\overline{M}$) of the product gases depends on the relative amounts of C, H, N, O, and other elements. If we compare DBRPs and composite rocket propellants (CRPs), it is seen that the I_{sp} of CRPs is more than that of DBRPs (see Table 6.1).

Although the average molecular weight of gaseous products is more in the case of CRPs because of the presence of chlorine, mainly as hydrogen chloride (molecular weight = 36.5 mole^{-1}; chlorine originating from the oxidizer, AP), the higher heat output due to the highly exothermic oxidation of aluminum (fuel) more than compensates for the molecular weight factor. On the other hand, composite modified double-base (CMDB) rocket propellants, which are an intelligent combination of CRP and DBRP (CMDB propellant uses an energetic polymer matrix based on a double base, i.e., NC and NG, in which AP and aluminum are incorporated), exhibit I_{sp} much higher than even those of CRPs. The major drawback of CMDB rocket propellants is their sensitivity to mechanical initiation due to the presence of NC and NG.

6.7.1.2. Burn Rate and Other Ballistic Parameters

A solid rocket propellant should burn at a specified LBR (r) at its operating pressure. The propellant chemist realizes that r depends on various factors, such as

1. The heat of explosion (to which it is directly proportional);
2. The presence/absence of a catalyst (e.g., Fe_2O_3 is used as a burn rate catalyst in some cases because it is believed to catalyze the decomposition of AP through an electron transfer mechanism setting out a host of free radical and ionic species that catalytically pyrolyze the polymer matrix);
3. The particle size and its distribution in the case of the oxidizer particles in CRPs and CMDB rocket propellants (generally, the lower the average particle size, the higher the specific surface area resulting in higher mass burn rate);
4. The presence of heat conducting substances (e.g., addition of carbon black); and
5. Erosive burning conditions.

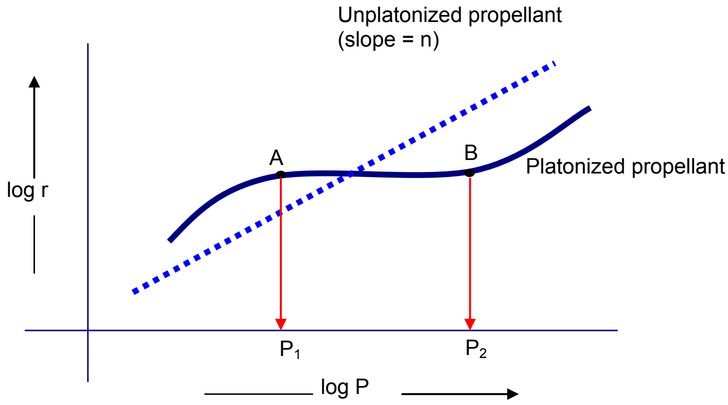


Figure 6.9
Plateau Effect.

Apart from burn rate catalysts, in some cases, certain substances need to be added in the propellant composition to ensure that the value of *r* does not change between certain pressure ranges. This is called a "plateau" condition, and the substances added for this purpose are called "platonizers" (see Figure 6.9).

Addition of platonizing agents, such as basic lead stearate in DBRPs, has been found to be effective in achieving a pressure independence of the burn rate between certain pressure ranges (P_1 to P_2). The value of the pressure exponent n is nearly zero in this region. Substances such as basic lead stearate, basic lead salicylate, etc., have been successfully used to achieve platonization in DBRPs.

6.7.1.3. Processability

While taking care of the energetics, the propellant formulator has to consider the processability of what he intends to formulate. He will have to carefully analyze the interdependence of various factors of processability and choose the most optimal formulation. Let us illustrate this with an example of a CRP formulation.

A CRP contains an oxidizer (mostly AP) and a metallic powder (e.g., aluminum powder) dispersed in a polymeric matrix (e.g., a polyurethane matrix that plays the dual role of binding AP and aluminum, thereby structural integrity to the propellant grain and a fuel). The formulation also contains smaller percentages of other ingredients such as a plasticizer, process aid, burn rate catalyst, etc. A typical composition is as follows:

1. AP = 68% (2:1 mixture of coarse AP ($\sim$250 μm) and fine AP ($\sim$10 μm)),
2. Aluminum = 17%,
3. Polymer = 15% (polyurethane, based on hydroxyl terminated polybutadiene (HTPB)), and
4. One part of Fe_2O_3 (burn rate catalyst).

The major steps involved are as follows:

1. Ingredient preparation
   a. Drying of AP and blending of the coarse and fine varieties (it is called “bimodal AP.” The purpose of blending coarse and fine AP is to achieve maximum loading of AP in the thick viscous “prepolymer”-like HTPB before the prepolymer is cured. Remember the mason mixing fine cement with sand particles of various sizes while making concrete mixture? Such a multimodal mixing ensures that the interstices between bigger particles are filled by smaller particles ensuring maximum space utilization).
   b. Drying of aluminum powder.
   c. Drying of HTPB, plasticizers, etc.
2. Mixing

   All of the above ingredients are mixed in a mixer.

3. Addition of curative

   The addition of curative sets in the curing reaction. In our example, addition of toluene di-isocyanate (TDI) starts the curing reaction (the NCO groups of TDI react with the terminal OH groups of HTPB forming the urethane, NH.COOR linkage between HTPB prepolymer molecules), and the slurry mix becomes more viscous.

4. Casting

   The slurry is cast into an inner-lined rocket motor fitted with a mandrel. (Note: The slurry should be poured/cast into the motor before its viscosity increases beyond a certain level.)

5. Curing

   The rocket motor into which the propellant slurry has been cast is kept in an oven, the temperature of which may be approximately 70 °C for approximately 7 days.

6. Mandrel removal after removal of the rocket motor from oven and cooling. The propellant curing process is over and the mandrel is carefully removed. After necessary inspection (e.g., X-ray inspection to ensure the absence of defects such as cracks and voids in the solid grain), the motor is ready for firing after further assembly.

Let us say that the above formulation realizes the following performance parameters:

$I_{sp} \cong 245$ s, burn rate $= 10$ mm s^{-1} at 70 kg cm^{-2}

If the propellant chemist is asked to modify the composition so as to increase the I_{sp} to 250 s without affecting the burn rate, then what options are left to them and with what consequences?

Option 1

Because I_{sp} is directly proportional to flame temperature and heat of explosion, they can go in for higher loading of AP and aluminum so that the solid loading goes from 85% to 87%.

Consequence 1

This 2% increase in solid loading is too much for the HTPB prepolymer to take. It becomes difficult to mix. Even if they manage to mix, the viscosity increase of the mix after the addition of curative is too fast for smooth casting. The propellant made out of this mix is very likely to contain many voids that are unacceptable.

Consequence 2

Higher AP and aluminum means higher flame temperature, which will increase the burn rate beyond 10 mm s^{-1}, which also is unacceptable.

Consequence 3

A lower percentage of the polymeric matrix in the final propellant will adversely affect the mechanical property of the propellant, leading to a lower percentage of elongation and a lower glass transition temperature.

Option 2

Increase the solid loading by 2% but compensate it by decreasing the ratio of finer AP so that viscosity increase can be taken care of.

Consequence 1

When the percentage of fine AP decreases (or that of coarse AP increases), the burn rate of the final propellant will decrease, which is not acceptable.

Consequence 2

A large increase in coarse AP percentage will also affect the mechanical property of the final propellant by reducing its tensile strength.

Option 3

Increase the solid loading by 2% but use the prepolymer HTPB of lower viscosity to take care of the viscosity build-up.

Consequence 1

Lower viscosity means lesser chain length/molecular weight of HTPB, and this will result in poor mechanical property of the final grain.

Consequence 2

A higher burn rate.

The above is just one example of the complex interplay of various parameters of formulation viz-a-viz the processability. The propellant chemist needs to blend chemistry and experience to solve such problems for which there are no quick-fix solutions.

6.7.1.4. Mechanical Properties

A rocket propellant grain has to withstand various mechanical stresses right from the time it is made until it is used. At various stages such as transportation, storage, assembly, and actual flight it undergoes tensile and compressive loads, shocks, vibration, high G values, etc., and if the mechanical properties of the grain are too poor to withstand such stresses, then it will result in the formation of abnormalities such as cracks, which are highly disastrous. In general, a propellant grain, which is free-standing and gets loaded to a motor after inhibition, requires a high tensile strength. In the case of case-bonded propellant charges (i.e., in which the propellant is directly cast into lined motors in situ), the grain should be able to take high compressive load and should therefore have higher elongation.

6.7.1.5. Storage Stability/Life

The rocket propellants, particularly meant for military use, are stored in assembled motors for a long period under varying conditions of temperature and humidity. The propellant chemist has to carefully analyze the compatibility among various ingredients that are used in propellant processing. For instance, an incompatible ingredient may accelerate the breakdown of the polymer matrix in a propellant, resulting in the development of cracks. There are well-established methods, such as several surveillance tests and thermal analyses, which can help in assessing such incompatibilities.

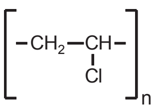
6.7.1.6 Safety and Environment: Cause for Concern

Safety is the most important factor that should be foremost on the mind of any HEM chemist. They are handling materials that have all of the three types of risks: explosion, fire, and toxicity. It is a known fact that under extreme conditions, such as undue confinement, a propellant or many of its ingredients can violently detonate. Fire risk is always there with any type of propellant. Quite a few chemicals used in propellant processing are carcinogenic and mutagenic. When the propellant is finally processed, it must be reasonably insensitive to impact, friction, and static discharge. There is no relevance in formulating a high-energy propellant that is quite dangerous to handle.

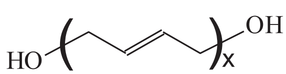
All over the world, the propellant scientists and technologists are exploring the possibility of going in for ecofriendly or “green” propellants and propellant ingredients. For example, despite many of its attractive properties (e.g., low cost, better energetics, and stability), AP is found to be ecologically detrimental when used in several tons. Large quantities of chlorine-related products emitted in the upper atmosphere when AP-based propellants burn cause environmental problems such as acid rain and ozone depletion. Efforts are on to replace AP with new, ecofriendly (chlorine-free) oxidizers such as ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF). The above are the major six factors that the propellant chemist must keep in mind while formulating a propellant for a given mission, apart from considerations such as cost and availability of raw materials.

6.8 Future of Rocket Propellants

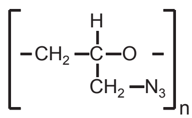
The progress in the field of rocket propellants has been painfully slow despite the enormous amount of research going on all over the world. This is primarily due to the conflicting conditions and requirements that confront propellant chemists, such as energetics, cost, safety, stability, and environmental friendliness. When a candidate propellant ingredient is synthesized, it is very exhaustively tested for all of these criteria before it can be introduced in a rocket propellant formulation. For example, it took several decades to replace the good old polyvinylchloride-based plastisol propellants with today's workhorse propellant that is based on HTPB. Many later versions of binders such as glycidyl azide polymer and oxetane-based polymers and copolymers containing energetic functional groups such as nitro, nitrato, and azido groups have their own disadvantages and still HTPB is reigning supreme. Despite the loud cries against the ecological impact of AP, it is still the most used oxidizer because of its many attractive properties. The alterative candidates have certain serious disadvantages. For example, HNF is still not safe enough for large-scale processing because of its high sensitivity to friction. ADN is not attractively energetic, and its high hygroscopicity poses problems for processing. The same argument applies when we search for better metallic fuels to replace aluminum. Beryllium gives more energy on oxidation, but the products are unacceptably toxic. Lithium is less energetic. On combustion, boron gives problematic products. Much research is going on all over the world in this direction, and we hope that we discover better oxidizers, fuels, plasticizers, burn rate catalysts, etc., in the foreseeable future so that we can aim for longer ranges and higher payloads in tomorrow's rockets.



PVC



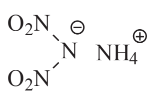
HTPB



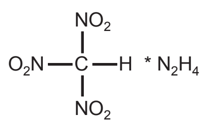
GAP

NH_4ClO_4

AP



ADN



HNF

PVC: Polyvinylchloride

HTPB: Hydroxyl terminated polybutadiene

GAP: Glycidyl azide polymer

AP: Ammonium perchlorate

ADN: Ammonium dinitramide

HNF: Hydrazinium nitroformate.

Suggested Reading

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[7] J.P. Agarwal, High Energy Materials, Propellants, Explosives and Pyrotechnics, Wiley, 2010.
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Questions

1. What are the two major parts of a solid rocket motor?
2. What is the role of a CD nozzle in a rocket motor?
3. Can you explain, using the thrust equation, why the thrust experienced by a rocket is maximal while it traverses through vacuum?
4. What are the relative merits and demerits of solid and liquid rocket engines?
5. Explain why the unit of specific impulse is expressed in seconds and how it is related to the exhaust velocity of gases.
6. Calculate the weight of a solid rocket propellant ($I_{sp} = 210$ s) that should be loaded in a rocket motor to produce a thrust of 6 tons. The propellant burns for 4 s (Answer: 114.3 kg).
7. What are the two major characteristics that decide the value of its specific impulse?
8. What are the factors that reduce the actual (realized) I_{sp} of the propellant compared with the theoretical I_{sp} calculated?
9. What is Vielle's law and why must a propellant chemist be worried about the value of n, the pressure index?
10. What is the significance of C^*?
11. Why is the job of a rocket propellant chemist similar to walking on a rope?

12. Why are CMDB propellants more energetic than the composite and double-base propellants?
13. What are the major steps involved in processing composite propellants?
14. Case-bonded rocket propellants should have high compressive strength and elongation. Why?
15. Name some of the potential candidates for polymeric binders, fuels, and oxidizers for use in solid rocket propellants.