1   Intro

This article provides an introduction to the composition and combustion of solid rocket propellant. As a new Rocket Team member, it should help you to:

-   understand the workings of solid rocket motors used by the Team, and
-   develop the technical background to contribute to the design and production of the Team's custom solid rocket motors.

The purpose of solid rocket propellants is to generate hot gas at high pressure. This gas is then expanded through a nozzle and ejected from the rocket motor to provide propulsive force. While other technologies exist to generate hot gas for rockets, solid propellants are preferred for certain applications because they are easily stored and usually enable propulsion systems to be mechanically and operationally simple.

A solid propellant generates hot gas by chemical reactions between the propellant ingredients. These reactions have (mostly) gaseous products and are highly exothermic. The chemical potential energy released by the reaction heats the products to high temperatures, typically 1500 to 3000 kelvin. Because these reactions involve the exothermic oxidation of a fuel by an oxidizer, they belong to the class of combustion reactions.

A solid propellant contains both fuel and oxidizer mixed together. This is different from most other combustion systems, where the fuel and oxidizer are only mixed just before combustion (e.g. internal combustion engines, torches, liquid bi-propellant rocket engines). Thus, a solid propellant can burn on its own; unlike a fuel (e.g. gasoline), it does not need an external supply of air or other oxidizer. This has clear benefits for a space propulsion system. However, it also poses a chemistry challenge: the propellant chemist must find a set of ingredients which react energetically with each other, but can also be safely stored and handled while mixed together. Clearly, a formulation which spontaneously ignites during mixing has no practical value as a storable solid propellant. A propellant must also not ignite when exposed to mechanical shock, heat or electrostatic discharges during handling. A propellant which is resistant to these accidental ignition sources is said to have low sensitivity. In chemical terms, low sensitivity roughly requires that the combustion reaction have high activation energy.

A further difference between solid rocket motors and most other combustion devices is that the motor contains all its propellant in the combustion chamber, rather than gradually injecting it as it is to be burned. This means that the rate of propellant consumption is not governed by a throttle or injector, but by the chemical dynamics of the combustion reaction. The propellant must burn at a stable and predictable rate. Formulation which react very quickly may be useful as explosives, but not as propellants.

This article specifically discusses a class of solid propellants called ammonium perchlorate composite propellants (APCP). Examples of composite propellants include:

-   Most high-powered hobby rocketry propellants
-   Most space-launch solid propellant rockets (e.g. the Space Shuttle's Reusable Solid Rocket Motor, Orbital ATK's Star motor series)
-   Rocket Team's Xaphan propellant

APCP contains a solid oxidizer (ammonium perchlorate) and (optionally) a powdered metal fuel, held together by a rubber-like binder. APCP is a good propellant choice because it is relatively safe and easy to produce, has low sensitivity, and has decent propulsive efficiency (up to ~270 seconds of specific impulse).

This article will explain APCP combustion starting with small-scale phenomena and progressively zooming out to encompass an entire motor. Starting at the micro-scale, we will discuss the propellant ingredients and their chemical behavior. Zooming out to the meso-scale, we will see how chemical behavior gives rise to the flame structure and the effect of pressure on the combustion process. Finally, at the macro-scale, we will see how the internal ballistics of a solid rocket motor determine its thrust and chamber pressure.

2 Propellant ingredients and their behavior

Composite propellants contain oxidizers and fuels in distinct solid phases. The typical oxidizers are crystalline solids with high oxygen balance, divided into small particles (10 to 500 µm) and dispersed though the propellant. A polymer matrix, the binder, binds the oxidizer particles together, giving the propellant mechanical strength. The binder serves as a fuel, giving off hydrocarbon vapors during combustion. Additional fuel may be added as hot-burning metal powder dispersed in the binder.
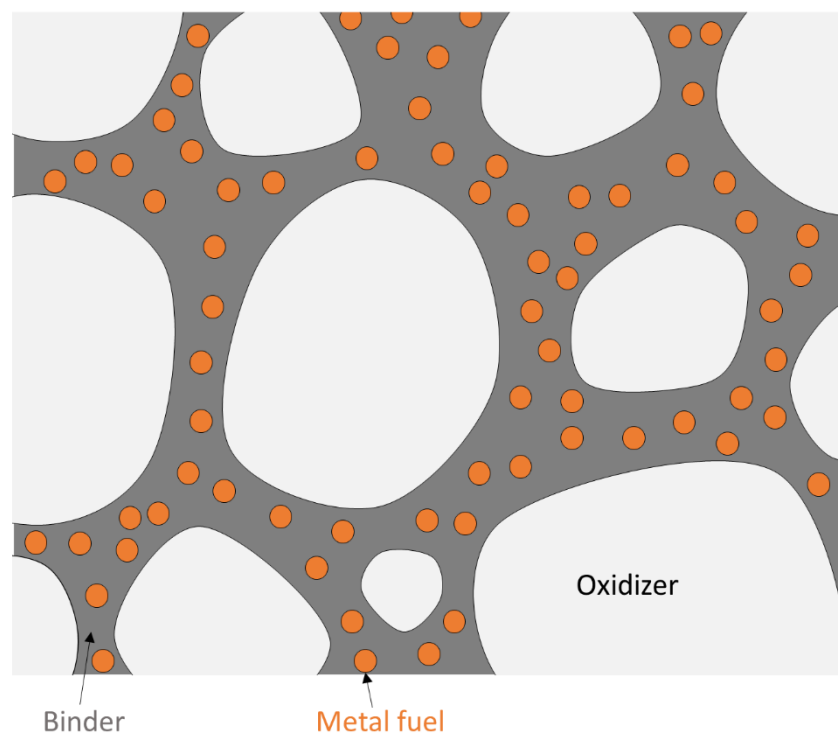
Figure 1: A composite propellant consists of crystalline oxidizer particles, and possibly a metal fuel powder, dispersed in a polymer binder.

2.1 Oxidizer: ammonium perchlorate

Ammonium perchlorate (AP, NH_4ClO_4) is the most commonly used oxidizer, and is preferred for the high flame temperature and specific impulse of propellants based on it [1]. Its exothermic decomposition

produces oxidizing species, such as O_2, Cl_2 and N_2O, along with H_2O, HCl, N_2 and other minor products [2].

At a high heating rate and high pressure, AP begins to melt at 720 K, and there can be a liquid layer on the surface of AP particles during combustion [2]. Because the net decomposition reaction is exothermic, AP can burn as a monopropellant (flame temperature of 1200–1400 K) at high pressures [2].

AP is a white crystalline solid at ambient conditions. For use in propellants, it is supplied as a powder with particle sizes typically between 15 and 500 μm.

Figure 2: Ammonium perchlorate powder

2.2   Binder: Hydroxyl-terminated polybutadiene

Several rubber-like binders can be used in composite propellants. Rocket Team's Xaphan propellant uses hydroxyl-terminated polybutadiene (HTPB). HTPB enables higher solids loading, which leads to a closer to stoichiometric oxidizer to fuel ratio, and has good mechanical and storage properties [3].

Uncured HTPB is an oligomer of butadiene [Figure 3], and is a viscous liquid at room temperature [Figure 5]. It is cross-linked into a solid polymer during propellant production, after solid ingredients have been mixed into the binder. Diisocyanates are used as curatives. An isocyanate ($-N = C = O$) group reacts with a hydroxyl group to create a urethane bond [4]. Diisocyanates have two isocyanate groups and can bond to two hydroxyl groups, creating a cross link between HTPB chains [Figure 4].

During propellant combustion, HTPB decomposes into a fuel-rich vapor, mostly CH_n and C_2H_n, which burns with AP decomposition products.
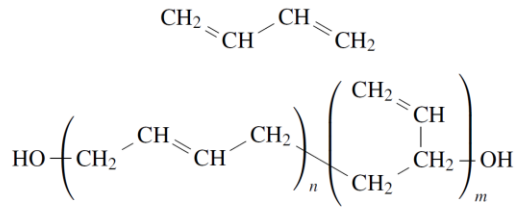
Figure 3: The 1,3-butadiene monomer and the HTPB oligomer. The oligomer has n cis and trans units and m 1,2 vinyl units. Note that the cis/trans and vinyl units may be interspersed. In typical propellant-grade HTPB, $m + n \approx 45$ and $m/n \approx 0.3$ [4].
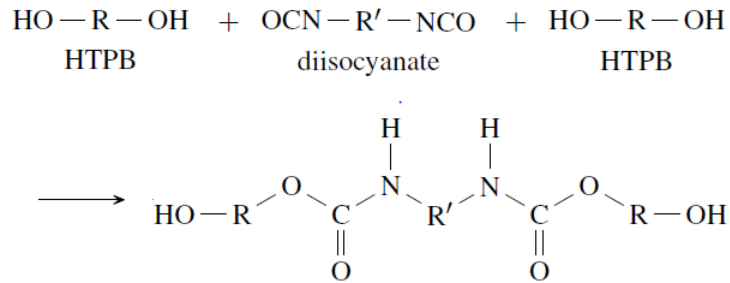

Figure 4: Diisocyanate cross-links HTPB.

The binder and oxidizer are typically mixed in a fuel-rich ratio. This ratio is chosen for reasons of performance and production. T_c is maximized by a propellant which has the stoichiometric ratio of oxidizer to fuel. Specific impulse, however, is maximized slightly fuel-rich propellants, because fuel-rich combustion has lighter exhaust species (i.e. H_2 and CO). However, propellants typically include more than the I_{sp}-optimal amount of binder for production reasons. At least 10-15% binder is required for a propellant which can be mixed and cast in slurry form, and which has acceptable mechanical properties once cured [3].

Figure 5: HTPB resin.

2.3 Metal fuel: aluminum powder

Metal powder, usually aluminum, is added to solid propellants to increase their flame temperature and specific impulse. It is supplied as a fine (< 50 µm) powder.

Figure 6: Aluminum powder

2.4 Minor ingredients

Other minor ingredients can be included in the propellant. *Opacifiers* (e.g. graphite powder or nigrosin dye [5]) make the propellant opaque and emissive, which improves radiation heat transfer to the

propellant surface and is necessary for good combustion. *Bonding agents* (e.g. HX-752) promote better adhesion between the oxidizer particles and the binder [6], improving mechanical properties and stabilizing combustion. *Antioxidants* (e.g. CAO-5) improve the shelf life of the propellant. *Surfactants* and *processing agents* (e.g. silicone oil, castor oil, Triton X-100) make mixing and casting easier by improving the rheological properties of the propellant slurry. *Burn rate suppressants* (e.g. oxamide) or *catalysts* (e.g. Fe_2O_3) can be added to modify the propellant's burn rate.

3   Combustion process and flame structure

The combustion process of a composite propellant has many steps, and the flame structure is complex. Although the propellant is a solid, important reactions, including combustion of the fuel with the oxidizer, occur in the gas phase. A set of flames hover over the surface of the burning propellant. These flames transfer heat to the propellant surface, causing its solid components to decompose into gases. The gaseous decomposition products contain fuel vapor and oxidizing species, which supply the flames with reactants.

Importantly, the combustion process contains a feedback loop. Heat from the flames vaporizes the surface, and vapor from the surface provides fuel and oxidizer to the flames. The rate at which this process proceeds depends on chemical kinetics, mass transfer, and heat transfer within the combustion zone. Importantly, the feedback rate depends on pressure. As we will see in the next section, the rate of propellant consumption determines the chamber pressure and thrust of a solid rocket motor.

3.1   Qualitative flame structure

The combustion process can be divided into 6 different reactions. The locations of several of these reactions are illustrated in Figure 7.

1. *Binder decomposition* – At the binder surface, heat flux from the flames warms the binder a decomposes it into a hydrocarbon gas. If a metal fuel is present, solid metal particles are ejected from the decomposing binder. This reaction is endothermic [4].
2. *AP condensed phase reactions* – At the surface of an AP particle, AP decomposes to give off gaseous, oxidizing products. A liquid melt pool forms on the surface of the AP as an intermediate step. This reaction is exothermic [2].
3. *AP monopropellant flame* – Some of the AP products (NH_3 and $HClO_4$) burn with each other in the gas phase close to the AP particle surface. This reaction is exothermic, and has a flame temperature of 1200 – 1400 K. The standoff distance between the AP flame and the propellant surface depends on the velocity of the product gases and the kinetics of the reaction [2].
4. *"Primary", or "leading edge" flame* – The primary flame burns close over the boundary between an AP particle and the surrounding binder. At the boundary, oxidizing vapors from the AP and hydrocarbon vapors from the binder are effectively premixed. This allows for a hot (~3000 K [7]), intense flame close to the surface. The primary flame standoff distance is mostly set by kinetics.
5. *Diffusion flame* – The diffusion flame is cooler and exists further from the surface. Oxidizer and fuel vapors which were not consumed by the primary flame diffuse toward each other, meeting at the stoichiometric surface of the diffusion flame. In fuel-rich propellants, it closes over the AP particle. As the name implies, the location and combustion rate of the diffusion flame are set by molecular diffusion.

6. *Metal droplet combustion* – Particles of solid metal fuel are ejected from the decomposing binder surface, and are warmed by passage through the flames. During this time, the particles agglomerate, melt into droplets, begin to boil, and ignite. Combustion occurs on a comet-shaped halo around the droplet. The metal droplets burn far from the propellant surface, roughly 2~200 mm [8] (compared to the ~500 μm height of the flame structure [7]). By the time the metal burns, most of the usual oxidizing species have been consumed by the primary and diffusion flames. Instead, the metal is oxidized by reducing H_2O and CO_2 in the exhaust to H_2 and CO [8].
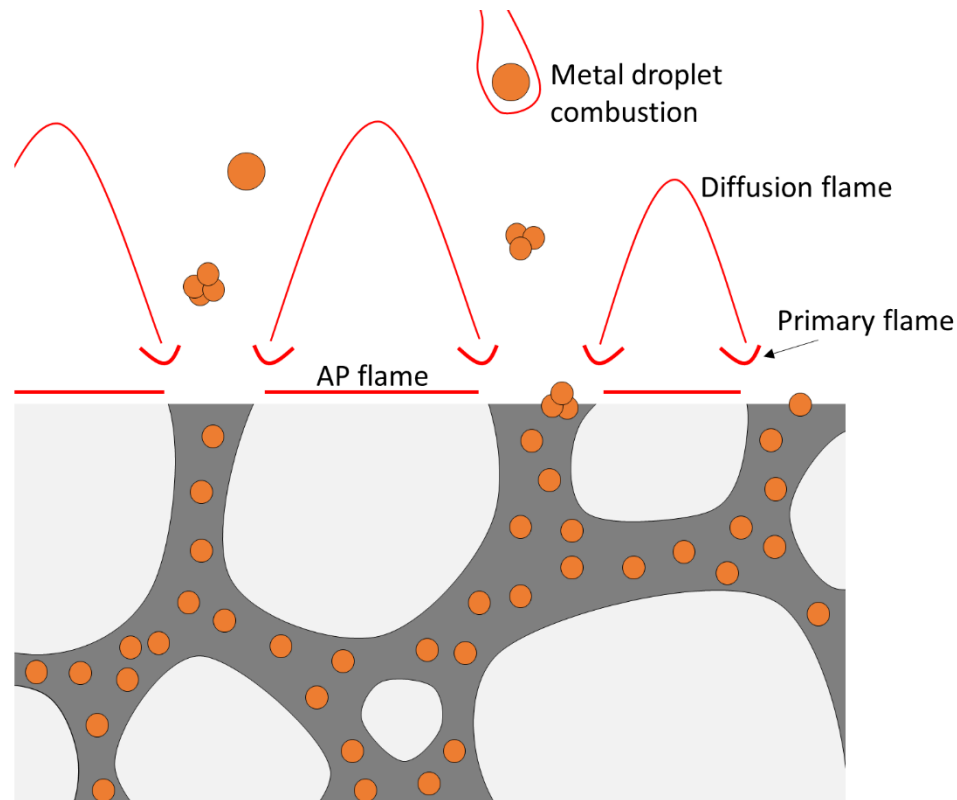

Figure 7: Flame structure over a composite propellant. Based on figures in [9] and [8].

3.2 Effect of chamber pressure on burn rate

The flame structure is important to understanding the behavior of propellants in a rocket motor. Specifically, it elucidates the effect of pressure on burning rate. At higher pressures, the gas phase is denser, causing reactions and diffusion to proceed more quickly. This moves the flame structure closer to the surface. The closer flames and denser conducing medium enhance heat transfer to the surface, which drives more decomposition, increasing the burn rate.

3.2.1 The Vielle model for burn rate

Although this dependence is complicated, it can be empirically modeled by Vieille's Law, which relates the burn rate r to the chamber pressure p_c via two parameters:

$$r = a\,(p_c)^n$$

r is the rate at which the surface regresses, and has units of velocity. a is the *burn rate coefficient*, which has units of $[velocity \times (pressure)^{-n}]$. n is the unitless *burn rate exponent*. The model parameters a, n must be determined by combustion experiments on the propellant.

While this model is commonly referred to as Vieille's "Law", it is important to remember that it is only an empirical approximation; it does not apply to certain propellants in certain propellant regimes. In mathematical terms, we can think of the Vieille model as a linearization in $\log(r)$ vs $\log(p_c)$ space:

$$\log(r) = \log(a) + n \log(p_c)$$

If we plot experimental data in log-log space, the data for some propellants will fall approximately in a line, and these propellants will be well-characterized by the Vieille model. Even if the data is not linear, we may be able to get away with using the linearization over a small range of pressures.

One deviation from Vieille's Law, plateau burning, is illustrated in Figure 8.
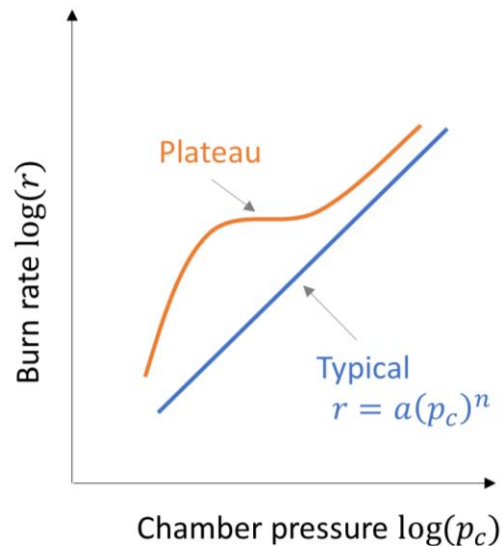

Figure 8: Typical propellants have a burn rate vs pressure dependence which forms a straight line on a log-log plot, and can be modeled by Vieille's Law. However, some propellants exhibit plateau burning, and cannot be modeled with Vieille's Law.

Further, many AP composite propellants do not have stable burning in rocket motors at chamber pressures above 14 MPa [10].

4   Motor internal ballistics

At the macro scale, the combustion process drives the behavior of solid rocket motors. The study propellant combustion and fluid dynamics within a rocket motor is called internal ballistics.

In a solid rocket motor, no throttles or other mechanisms exist to control the chamber pressure and thrust. Rather, the equilibrium chamber pressure of a solid rocket motor arises from the balance of exhaust generation from combustion and exhaust discharge through the nozzle. The propulsion engineer must understand internal ballistics to design a motor and propellant which will operate at the desired chamber pressure and thrust.

4.1   Equilibrium chamber pressure

The relation of burn rate and chamber pressure can be used to model the evolution of chamber pressure within solid rocket motor. Begin by applying the Ideal Gas Law to relate the chamber pressure p_c to the mass of gas present in the combustion chamber, m.

$$p_c = m\,R\,T_c\,\frac{1}{V_C}$$

where R is the specific gas constant of the combustion gases in the chamber, T_c is their temperature, and V_c is the chamber volume[1]. Assume that the gas in the chamber is sufficiently homogenized that it may be described by a single pressure, temperature and gas constant. Gas mass is added to the chamber by burning propellant, and mass flows out of the chamber through the nozzle. The rate of change of the chamber gas mass is

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out}$$

Now, find expressions for the mass flow terms. Isentropic nozzle theory [16] gives the mass flow through the nozzle as:

$$\dot{m}_{out} = \frac{p_c\,A_t}{c^*}$$

where A_t is the nozzle throat area, and c^* is the *characteristic velocity* of combustion gas, equal to:

$$c^* = \frac{\sqrt{\gamma\,R\,T_c}}{\gamma\sqrt{\left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}}}$$

The gas supplied by the propellant is

$$\dot{m}_{in} = A_b\,\rho_s\,r(p_c)$$

where A_b is the burn area of the propellant, and ρ_s is the solid propellant density.

Note that the nozzle flow is linear in chamber pressure. If the burn rate r is sublinear in chamber pressure, then there exists a stable chamber pressure where

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} = 0$$

The equilibrium pressure is given by:

$$p_c = K\,\rho_s\,r(p_c)\,c^*$$

$$K \stackrel{\text{def}}{=} \frac{A_b}{A_t}$$

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[1] The available chamber volume changes as solid propellant is consumed. Assume that this change is negligibly slow compared to the rates considered here.

Below this pressure, combustion flow exceeds nozzle outflow, and the pressure rises. Above this pressure nozzle outflow is exceeds combustion, and the pressure falls.

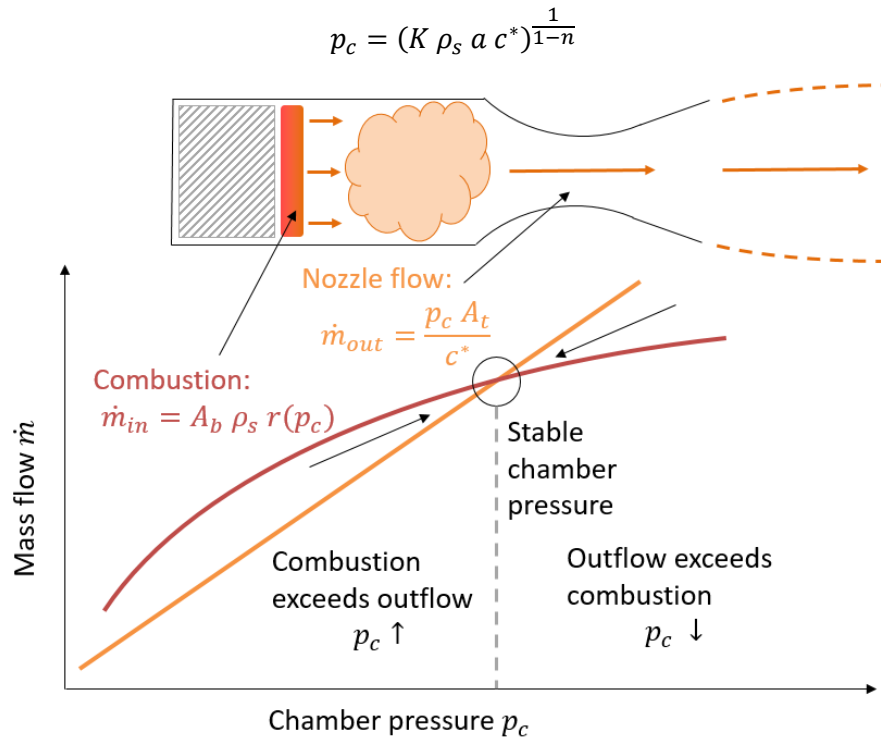If the propellant obeys Vieille's Law, the equilibrium chamber pressure can be written in closed form:

$$p_c = (K \, \rho_s \, a \, c^*)^{\frac{1}{1-n}}$$

Figure 9: The chamber pressure of a solid rocket motor arises from an equilibrium between gas generation by combustion and gas expulsion through the nozzle.

The next section gives more details on how these values are selected. It applies the concepts of this chapter to the design of a solid rocket motor which operates at a particular chamber pressure and thrust level.

4.2 Design for chamber pressure and thrust

New rocket designs must achieve a target thrust and chamber pressure to comply with mission requirements and structural limitations. However, the solid rocket motor does not have controls (e.g. pumps and valves) which can adjust the pressure and thrust. Rather, the chamber pressure and thrust are determined by the propellant combustion process and the motor geometry. The motor must be designed so that the internal ballistics will equilibrate at the correct pressure and thrust level.

The preliminary motor design process uses 5 variables. Two depended variables must be matched to their required values:

1. p_c, the chamber pressure, and
2. F, the thrust force.

Three independent variables may be adjusted by the designer to set the pressure and thrust:

3. A_b, the burn area of the propellant grain,

4. A_t, the area of the nozzle throat, and
5. a, the burn rate coefficient of the propellant.

There are two caveats on this statement of the design space:

1. Capturing the entire combustion process in a single parameter a is an aggressive simplification. Other properties the propellant (n, ρ_s, c^*, γ) also affect the pressure and thrust. Further, the relation between propellant burn rate and pressure may have plateaus which are not captured by the Vieille model ($r = ap^n$) [17]. However, to reduce complexity, this section neglects these effects. It is assumed that the propellant designer has a family of propellants which offers a range of a values at similar (n, ρ_s, c^*, γ), and fits the Vieille model near the design pressure. Oxamide-doped AP composite propellants, described in Sections **Error! Reference source not found.** and **Error! Reference source not found.**, provide such a propellant family.
2. These variables may not take on a single value, but instead evolve over time as the motor burns. For now, consider designing for a single point in the burn profile: perhaps just after ignition, or at the peak of the pressure trace.

Imagine the motor design space as 3-space parameterized by the independent variables A_b, A_t, a. Contours of p_c and F are surfaces in this space. The task of motor design is to find a point (A_b, A_t, a) which lies on both the desired pressure surface and the desired thrust surface. The two surfaces intersect along a curve; many valid design points are possible. The intersection curve lies in a plane of A_t, particularly the plane where

$$A_t = \frac{F}{p_c C_F(p_c, p_e, \gamma)} = \frac{F}{p_c \sqrt{\frac{2\gamma^2}{\gamma-1}\left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}\left(1 - \left(\frac{p_e}{p_c}\right)^{\frac{\gamma-1}{\gamma}}\right)}}$$

In this equation, $C_F(p_c, p_e, \gamma) \overset{\text{def}}{=} \frac{F}{A_t \, p_c}$ is the thrust coefficient of the nozzle. A pressure contour and its intersection curve with a thrust contour are illustrated in Figure 10.
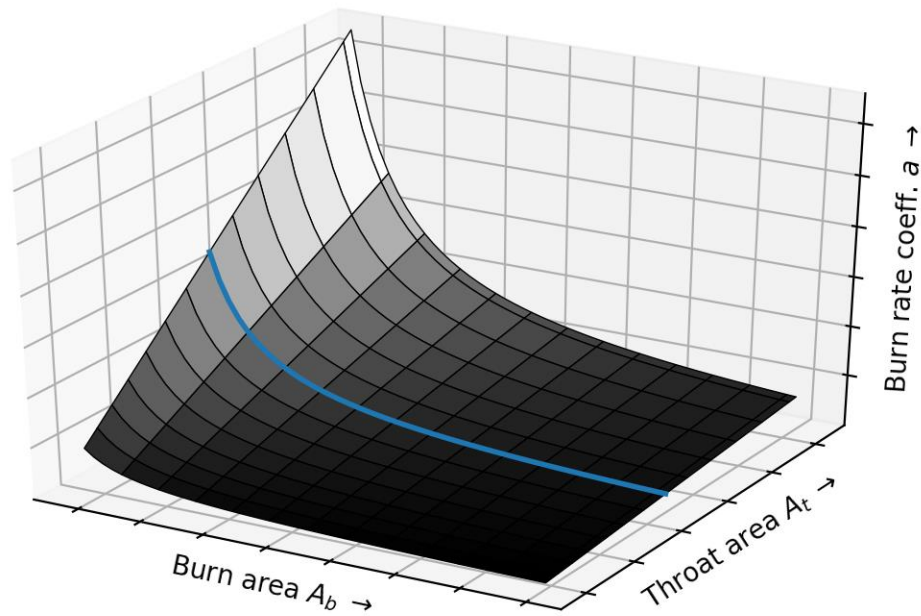
Constant-pressure surface

Figure 10: A surface of constant pressure in (A_b, A_t, a) space (grey), and its intersection with a particular thrust level (blue).

It is possible to simplify this relation. Recall from the previous section that the chamber pressure depends not on the distinct values of A_b and A_t, but on their ratio:

$$K \stackrel{\text{def}}{=} \frac{A_b}{A_t}$$

$$p_c = (K \, \rho_s \, a \, c^*)^{\frac{1}{1-n}}$$

This relation is illustrated in Figure 11. p_c increases with increasing a and increasing K. Motors with faster burning propellant, or more burn area compared to their throat area, will have higher chamber pressure.
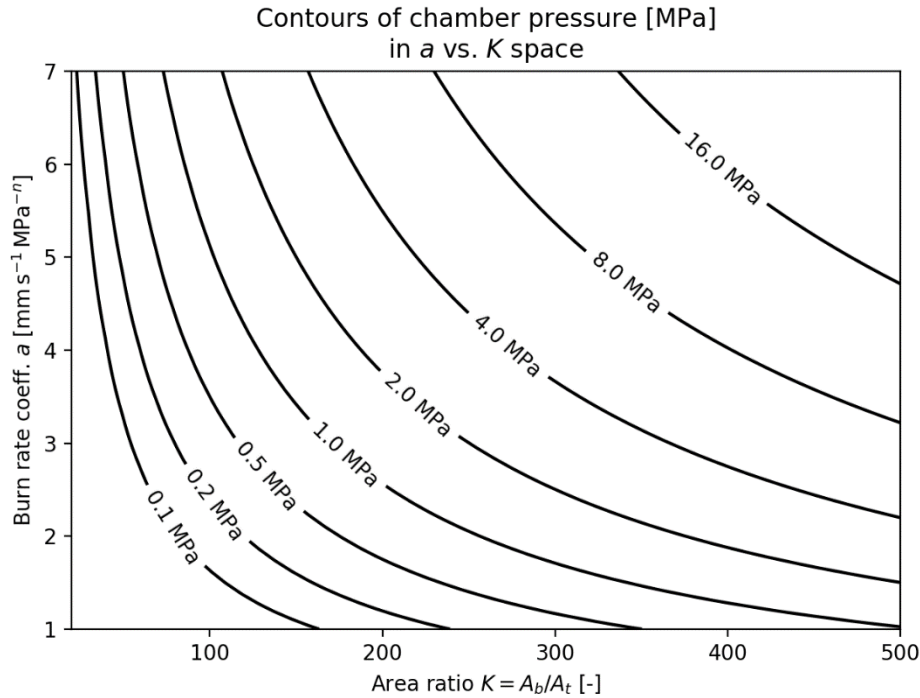
Figure 11: The chamber pressure of a solid rocket motor is set by the burn rate and the burn area / throat area ratio. This plot assumes a propellant family with $n = 0.45$, $\rho_s = 1500\ kg\ m^{-3}$, $c^* = 1300\ m\ s^{-1}$.

As currently formulated, the motor design problem is under-constrained. As shown above, the thrust and pressure constraints intersect along a curve, so many valid design points will fulfill both of them. A third constrain must be introduced.

In this typical motor design process, this constraint is introduced by selecting a particular propellant, with a known a value. Then, the motor designer must choose A_b, A_t to give the required pressure and thrust. This reduced design space is illustrated in Figure 12. The figure assumes a value for a, and plots contours of pressure and thrust on axes of burn area A_b versus throat diameter d_t. A motor designer would find the intersection of the desired pressure and thrust contours, read off the corresponding A_b and d_t, and design a motor with that geometry. If the geometry was not feasible within structural and packaging constrains, the process could be repeated with a different propellant. Most motor producers maintain a library of propellant compositions (order of 10 compositions) [15] [26]. These propellants provide a sufficient selection of burn rates (and other properties) to cover typical missions.
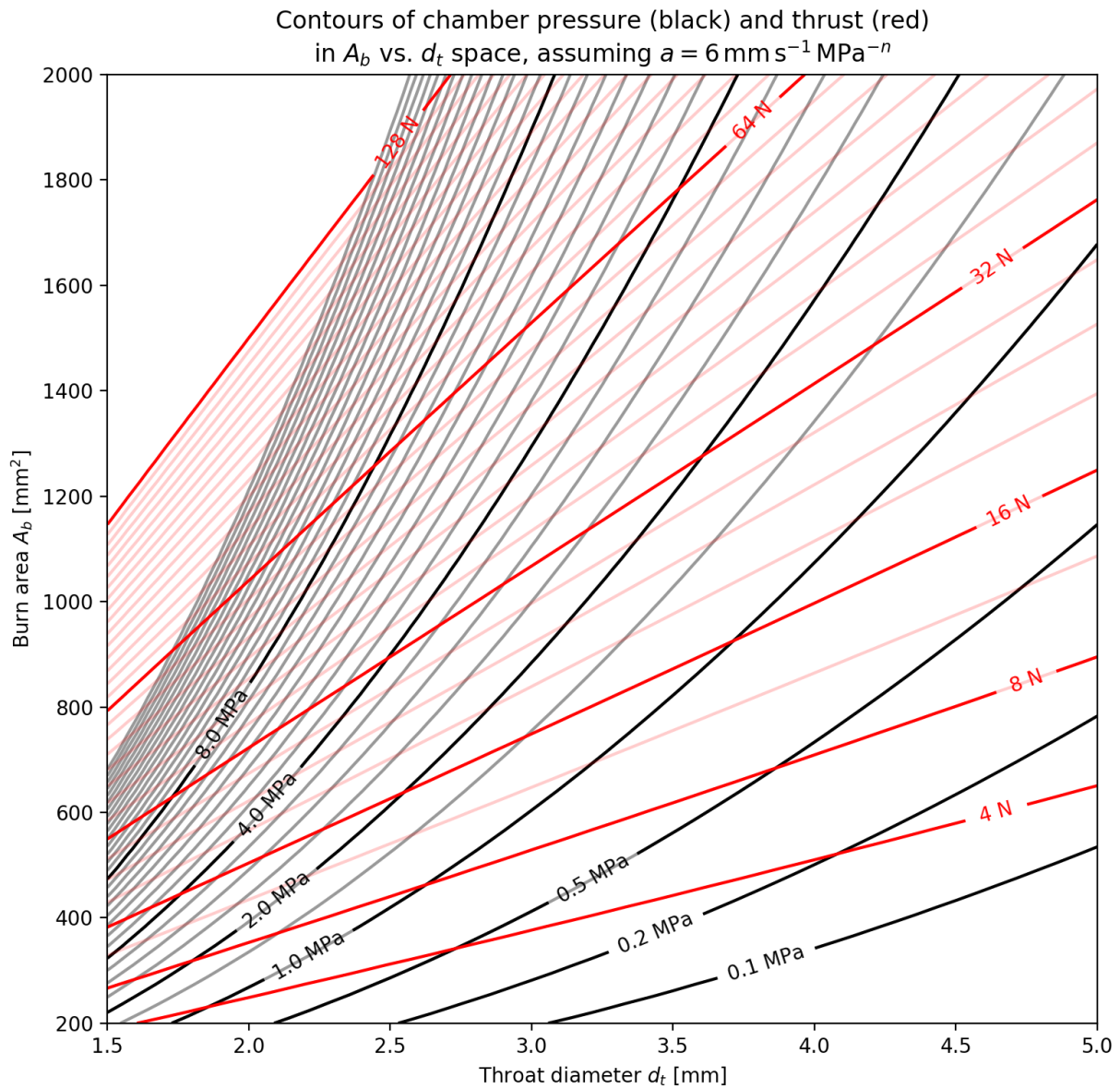
Figure 12: For a motor with fixed propellant burn rate coefficient a, the chamber pressure and thrust are set by burn area and the throat diameter. This plot assumes a propellant with $n = 0.45$, $\rho_s = 1500\ kg\ m^{-3}$, $c^* = 1300\ m\ s^{-1}, \gamma = 1.26$, and expansion to $p_e = p_a = 30\ kPa$. Minor lines show increments of 0.5 MPa and 4 N.

4.3   Burn area evolution and thrust curves

The surface of the propellant grain regresses as it burns [Figure 13]. If the area of the burning surface changes as it regresses, this will cause the chamber pressure and thrust of the motor to vary as well. The variation of thrust (or chamber pressure) with time is called a thrust curve. Thrust curves are classified as regressive (decreasing with time), neutral or progressive (increasing with time) [Figure 15].
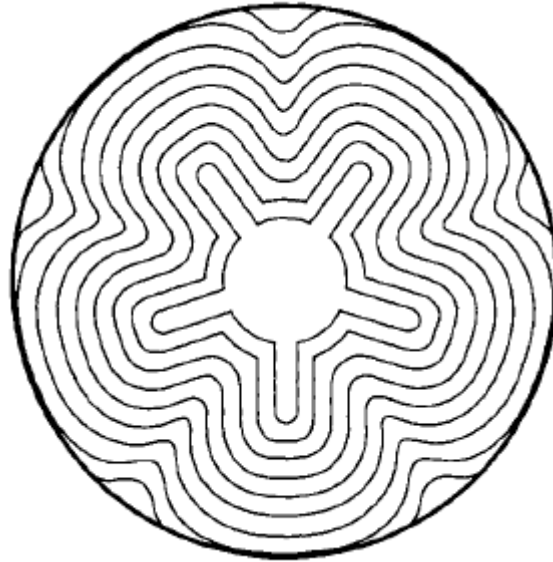
Figure 13: A cross section through a propellant grain, showing successive burning contours, each a fixed small time apart. The internal cavity grows with time. Reprinted from [3].
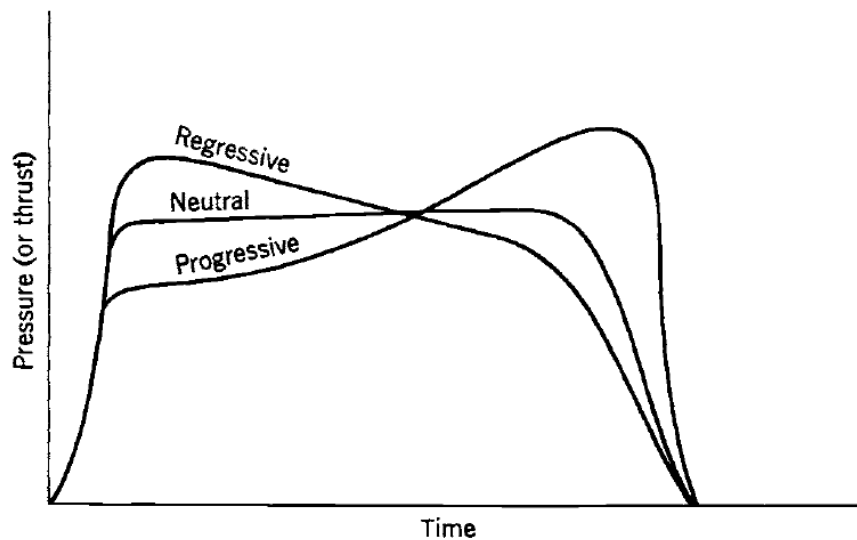

Figure 14: Classification of grains according to their pressure-time characteristics. Reprinted from [3].

A mission may require a particular thrust curve. The motor designer must then design a propellant grain geometry which will yield the desired thrust curve. Many grain geometries are possible [Figure 15]. The most popular grain geometry in high-powered amateur rockets is the BATES grain: a hollow cylinder of propellant which burns on the ends and inner surface. BATES grains are easy to manufacture, and have approximately neutral thrust curves if the length to diameter ratio is correct (TODO value).

Software tools such as burnsim (http://www.burnsim.com/) can predict the thrust curve for a given grain geometry, and are a useful aid in the grain design process.
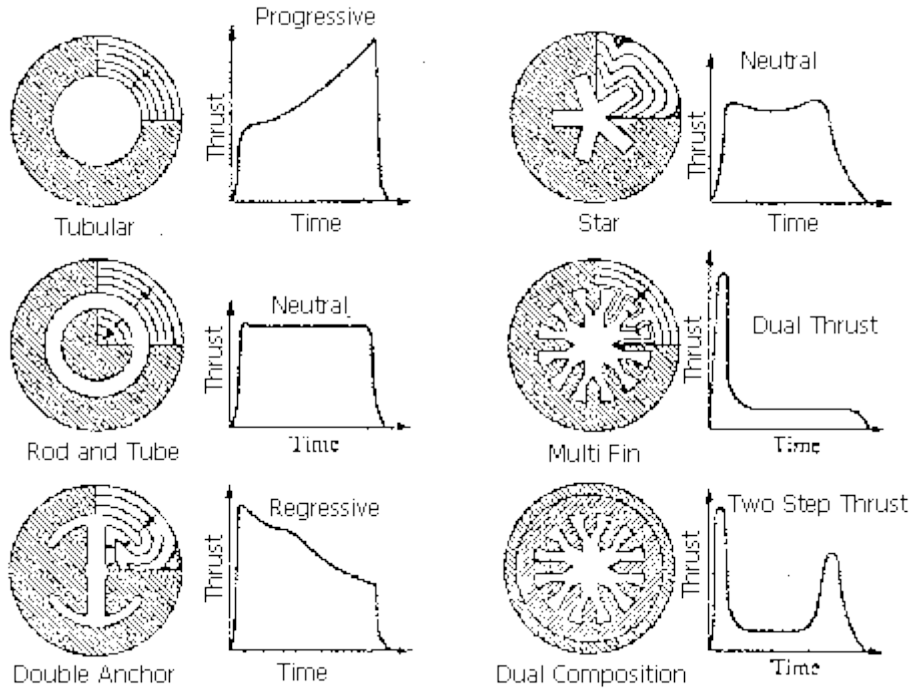
Figure 15: Various grains and their thrust curves. Reprinted from [13].

Figure 16: BATES grains of solid propellant.

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