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# Dieseling in Spring Piston Airguns A Conceptual Analysis

## Domingo Tavella, Ph.D.

# 1.0 Summary

Lubricating oil combustion in the compression chamber of a spring-piston air gun has a significant impact on the internal dynamics and on the performance of the gun. Using a well-known hydrocarbon (n-octane) as a proxy fuel for the lubricants that cause dieseling, this analysis reveals that a spring piston air gun responds to dieseling by delivering higher muzzle energy to the projectile in a non-linear relationship with the amount of fuel burnt - the grater the amount of lubricant burnt, the less efficient the transfer of combustion energy to the projectile. Dieseling causes substantial rises in peak temperatures and, depending on the ignition characteristics of the fuel, it mal also cause significantly higher pressure peaks within the compression chamber. For typical operating parameters, computations suggest that practically all the hydrocarbon is consumed before the projectile undergoes any significant movement within the barrel. Combustion happens extremely fast, with all the available fuel (or oxygen in a rich mixture) being exhausted within a small fraction of a millisecond.

# 2.0 Introduction

This work builds on my previous research in Ref. (1) - if you are not familiar with the internal working of a spring-powered air gun, you will benefit from reading at least the introduction in Ref. (1).

I refer to this analysis as "conceptual" because it is intended, by working within a highly stylized framework, to achieve a better understanding of the phenomenon rather than to predict precise results, and because some of its conclusions are open to rigorous experimental verification. These caveats notwithstanding, much of what the analysis reveals is in line with observations<sup>1</sup>.

As was the case with my work in Ref. (1), one of my objectives is educational. The problem we will discuss should appeal to advanced undergraduate or graduate students in engineering interested in seeing the interaction of chemical reactions and mechanical components in action. In addition, the problem also poses some interesting challenges in numerical analysis, bringing to light the issue of stiffness in ordinary differential equations.

<sup>1.</sup> In aerodynamics and fluid dynamics it is not uncommon to conduct studies within extremely stylized frameworks - ideal inviscid airfoil theory being one of the most prominent and useful examples.

When the piston seal or the chamber of a spring piston air gun is newly lubricated, the gun experiences a phenomenon commonly known as "dieseling". Dieseling occurs when some of the newly-applied oil reacts explosively with air in the compression chamber during the firing cycle. When dieseling happens, projectile velocities are often significantly higher, occasionally significantly lower, always more erratic, and the gun experiences higher vibration. When as a result of dieseling the projectile leaves the muzzle at supersonic speeds, accuracy degrades dramatically. The number of shots affected by clearly perceptible dieseling is usually small compared with the number of shots between lubrications<sup>1</sup>.

Another form of so-called dieseling in air guns occurs when a small amount of oil is deposited in the rear end of a pellet and the pellet is fired. This unwise practice is *not* the phenomenon we will discuss here, nor is it a particular case of our problem<sup>2</sup>.

To what extent the dieseling phenomenon is limited to the compression chamber or whether it also extends through the breach into the barrel behind the pellet has been the subject of some speculation, but no scientific evidence in the open literature seems to be available. The calculations I will discuss below show that the vast majority of the combustion takes place in the chamber, with a small fraction of fuel burning past the breech after the pellet has started moving.

As mentioned, dieseling is usually evidenced by a significant *increase* in muzzle velocity, and occasionally by a substantial *decrease* in muzzle velocity. The latter occurs when a gun has just been freshly and generously lubricated, or by dropping a little oil directly into the compression chamber through transfer port. Our focus will be on the former case, when oil combustion increases the pellet velocity. I will not speculate why the presence of oil in the compression chamber can sometimes cause a drop in the pellet velocity, beyond pointing to what appears to be a differentiated regime, likely involving detonation, a situation that cannot be handled by our current quasi-steady uniform framework.

The combustion regime we are interested in is a case of uniform auto-ignition in an environment with rapidly increasing temperature and pressure. Precise analysis of this phenomenon is a complex undertaking that would require a full solution of the reactive compressible Navier-Stokes equations, coupled with the dynamics of the spring, the piston, and the projectile. This exploration is a much simpler approach that builds on the work in Ref (1), with the objective of gaining a conceptual understanding of how dieseling affects projectile energy and the dynamics of the internal gun's components.

Modeling the combustion of lubricating oils is complicated even under the simplifying uniformity and quasi-steady assumptions in Ref (1). The reason is that you don't know the exact chemical composition of the lubricant, and even if you knew its composition, computing the energy released by the lubricant during combustion in an environment where pressure and temperature are rapidly varying is a demanding modeling task.

<sup>1.</sup> At least one commercially-produced air gun, the Weihrauch Barakuda EL54 ether-injected air rifle, purposely exploited this phenomenon to increase power.

<sup>2.</sup> This version of dieseling cannot be dealt with in the quasi-steady, diffusion-free framework used here.

Since precise combustion modeling, even ignoring non-uniformity, requires tracking a large number of species, something beyond the scope of this work, we must look for simpler alternatives.

The simplest approach is to assume a given amount of lubricant burns at a given temperature and pressure. The issue with this approach is that auto-ignition is preceded by a time period, referred to as induction time or pre-ignition delay, before the reaction flares up, which is itself a function of temperature and pressure. Although information exists about pre-ignition delay in lubricant combustions at different temperatures and pressures (Zabetakis, Ref (2)), this information doesn't easily translate into ignition times when the pressure and temperature are rapidly changing.

Another alternative is to use a "proxy" fuel, for which the combustion chemistry is well understood, to replicate the effect of lubricant combustion - this is the approach I will consider here. One economical way to implement the combustion chemistry of a proxy fuel is to replace the complex system of reactions with a single global reaction (Westbrook, Ref (3)). Replacing the complex system of reactions and species that evolve during combustion with a simple one-step model requires calibrating reaction parameters such that the simplified set-up can mimic a far more complex system. The calibration problem, however, is an inverse problem and a such is ill-conditioned. This means the calibrated parameters are functions of the problem used in estimating model parameters (Zanoni, Ref (4)).

I will use n-octane  $(C_8H_{18})$  as a proxy fuel. This does not mean I argue that n-octane is an exact stand-in for the details of the complex chemistry of lubricating oil combustion. I will argue, however, that any proxy fuel that burns explosively in the compression chamber will shed light on what actually happens during dieseling. In an earlier version of this work I used propane as a proxy fuel, but n-octane seems to better reflect the behavior of the pressure in the combustion chamber. The reason for using n-octane is that reliable data is available for one-step reaction modeling. The data, however, is for low-pressure flame propagation and you shouldn't expect that the calibrated parameters will apply precisely to air gun dieseling, where pressures are high and time-dependent. However, it is reasonable to expect that this approach will help us understand a complex problem.

An immediate question is the following: can any amount of lubricating oil cause dieseling, or is there a minimum below which no dieseling occurs? This question has a bearing on the role of lubricant combustion as a source of pellet energy during regular firing, not just during the relatively brief period when clearly identifiable dieseling occurs. Old lore among air gun enthusiasts has it that lubricant combustion contributes significantly to pellet energy over thousands of shots, even when dieseling is not clearly felt. There is no scientific evidence of low-level combustion in air guns in the open literature. Cardew and Cardew (Ref. (5)) report sustained power gains of the order of 50% of the air gun power due entirely to dieseling, but their experimental set-up is far from scientifically reliable and they do not report on data gathering, processing, and error analysis.

Although it is very difficult to establish the precise minimum amount of lubricant oil burnt during firing cycles, we can make educated estimates of the order of magnitude involved. Oiling the seal and compression chamber of an air gun involves applying just one or two

small drops of specially formulated lubricating oil every several thousand shots. Lubrication is applied from a small plastic container fitted with a very thin metal tube. The small size of the metal tube and the surface tension of the oil result in drops that weigh anywhere from 5 to 10 milligrams each. The size of these small drops is significantly smaller than the size of a "standard" drop. A standard drop is a pharmaceutical unit of measure equal to 0.05 ml. The small lubricant drops in an air gun are therefore from five to ten times smaller than a standard drop, assuming the density of oil being of the order of 1 g per ml.

The US Bureau of Mines has sponsored the study of ignition and explosions of lubricant vapors. As discussed in Zabetakis, Ref (2), the minimum concentration of lubricating oil vapor needed to form a flammable mixture with air at atmospheric temperature and pressure is approximately 48 mg per liter - this quantity decreases at higher temperature and pressure, probably significantly so. The relevant reference volume in an air gun when combustion occurs is the volume ahead of the piston when the piston is very close to the end of the chamber (the reason for this, as we will see below, is that combustion happens very close to the end of the piston stroke.) The smallest volume where combustion can take place is the volume of the transfer channel plus any cavities in the front of the seal (see Ref. (1) for details). A typical air rifle compression chamber is about 100 mm long and 25 mm in diameter, which corresponds to a volume of about 0.05 liters. Such a gun has a transfer port 3.4 mm in diameter and a transfer channel 23 mm in length, plus extra space in front of the seal which amounts to about 0.53 mm of the chamber length. The total volume of transfer channel plus seal cavities, therefore, amounts to about 0.00047 liters. This means that at room temperature and pressure the minimum amount of oil needed to have a flammable mixture in such a small volume would be about 0.025 mg.

Since gas in the compression chamber reaches pressures close to 30 kpa and peak temperatures of order 1,500 K, it is reasonable to assume the lower bound for auto-ignition could be less than 0.025 mg. How much pellet energy can we derive from such a small amount of lubricant? Assuming the heat released by combustion of one gram of lubricant to be 42 kJ, 0.025 mg of lubricant would generate about 1 J of power (remember that the heat *released* by combustion is the heat of reaction with *negative sign* - to prevent confusion I will use the terms *heat released* rather than *heat of reaction*). We will see later that only about a third or less of the power generated by lubricant combustion can translate into added pellet velocity. If this line of reasoning is correct, this tells us that the smallest possible amount of lubricant that can burn in the combustion chamber would impart to the pellet an extra 0.3 J of energy. This would be tiny by the standards of a firearm, where projectiles achieve muzzle energies of thousands of Joules, but in the case of a competition air gun firing pellets with 20 J of energy or less, this small amount translates into a velocity change of the same order as the standard deviation of the gun's muzzle velocity<sup>1</sup>.

The framework in Ref (1) assumes the flow within the compression chamber is quasi-stationary and uniform. I will expand this framework by adding the assumption that the combustion process in the chamber is uniform and kinetically controlled. This implies there

<sup>1.</sup> For a 10.34 gr pellet fired at 20 J, a 0.3 J change results in about 2.5 m/s muzzle velocity change.

are no species gradients in space, there is no diffusion, there is perfect mixing before ignition happens, and the reaction is irreversible.

Species will be allowed to be convected through the transfer channel into the barrel behind the pellet, thus allowing for combustion to continue past the breech. Calculations will show that by the time the pellet begins to move, in the case of a lean mixture, well over 95% of the proxy fuel will have been consumed (a rich mixture undergoes a similar process vis-a-vis the oxidant).

### 2.1 Combustion modeling

In the following kinetically-controlled reaction,

$$n_a A + n_b B \to P$$
 (EQ 1)

A and B are reactants, P are reaction products, and  $n_a$ ,  $n_b$  are stoichiometric coefficients.

A represents the fuel and B the oxidant. In the ideal case where the reaction products are the direct result of collisions between A and B molecules with no intermediate reactions or species, EQ 1 is referred to as an *elementary reaction*, and collision theory leads to the following coupled differential equations for the molar concentrations of the reactants,

$$\frac{\mathrm{d}}{\mathrm{d}t}[A] = -n_a k[A]^{n_a}[B]^{n_b} \tag{EQ 2}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[B] = -n_b k[A]^{n_a}[B]^{n_b} \tag{EQ 3}$$

where k is a function of temperature with Arrhenius form

$$k = F \exp \frac{-E_a}{R_u T} = F \exp \frac{-T_a}{T}$$
(EQ 4)

Here, F is referred to as the pre-exponential factor,  $E_a$  is the activation energy,  $R_u$  is the universal gas constant, T is the local temperature of the gas mixture where the reaction takes place, and  $T_a$  is the activation temperature.

Collision theory also says that the pre-exponential factor is a very large number (of order

 $10^{14}$ ), and that the activation temperature is much larger than ambient (in the tens of thousands K). This means that *k*, which defines the speed of the reaction, results from the product of a very large number and a very small number, one of which is changing very rapidly. This fact causes the rate of change of fuel and oxidant concentrations to remain almost constant for some time and then change extremely rapidly, as the temperature rises both due to the heat released by the reaction and the compression work done by the piston. In actuality, the fuel and oxidant do not react through simple collisions of *A* and *B* molecule, but rather through the formation of a large number of intermediate species, eventually leading to the products *P*. When this happens, solving the reaction problem requires solving a large system of coupled elementary reactions. In such a case, EQ 1 must be interpreted as short-hand notation for a complex system of reactions. This short-hand notation is also referred to as a *global reaction*. In such a case, EQ 2, 3, and 4 *do not* apply as written.

It is possible, however, to replace the  $n_a$ ,  $n_b$ ,  $E_a$  (or  $T_a$ ), and F parameters with calibrated quantities, such as to treat the global reaction as if it were an elementary reaction. Using calibrated exponents a and b, as well as a calibrated function k, equations

$$\frac{\mathrm{d}}{\mathrm{d}t}[A] = -n_a k[A]^a [B]^b \tag{EQ 5}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[B] = -n_b k[A]^a [B]^b \tag{EQ 6}$$

will mimic, at least to some extent, the far more complex system of reactions that actually take place.

Calibrating these parameters requires matching the results of precisely specified computational fluid dynamic experiments carried out with a comprehensive set of species, or through careful lab measurements. With this, a so-called *single step* approximation (Westbrook Ref (3)) can replace a complex system of reactions. A single-step approximation violates the actual chemical path of the reaction, but provides a means to visualize what happens without the burden of fully-fledged chemistry. There is the important caveat of ill-conditioning, however, and results must be interpreted with caution<sup>1</sup>.

#### 2.2 Conservation equations

It is cleaner to derive the conservation equations for generic species A and B in EQ. 5 and 6, and then specialize them to a specific proxy hydrocarbon. Let  $M_X$  denote the mass fraction of species X, where X stands for A or B. If  $\rho$  is the global density of the gas mixture where the reaction takes place (combustion is in air, which mean the gas mixture includes nitrogen), and  $\rho_X$  is the partial density of species X, the mass fraction of species X is

$$M_X = \frac{\rho_X}{\rho} \Longrightarrow \rho_X = \rho M_X \tag{EQ 7}$$

<sup>1.</sup> Ill-conditioning appears in a number of disciplines when you try to fit parameters to a complex problem where you postulate a solution structure to a simplified version of the problem.

The quantity  $\rho_X$  is the molar concentration [X] multiplied by the corresponding molecular weight,  $W_X$ . The relationship between species molar concentration and mass fraction is therefore,

$$W_X[X] = \rho M_X \Longrightarrow [X] = \rho \frac{M_X}{W_X}$$
 (EQ 8)

which yields the following relationship among the time derivatives,

$$\rho \frac{\mathrm{d}M_X}{\mathrm{d}t} = W_X \frac{\mathrm{d}}{\mathrm{d}t} [X] - M_X \frac{\mathrm{d}\rho}{\mathrm{d}t}$$
(EQ 9)

**Rate of species consumption.** Under the assumption of uniformity, the time rate at which mass of reactant species X is consumed in a volume V is  $q_X V$ ,

$$q_X = W_X \frac{\mathrm{d}}{\mathrm{d}t} [X] \tag{EQ 10}$$

$$q_X = -W_X n_X k[A]^a [B]^b$$
(EQ 11)

where  $q_X$  has dimensions  $\frac{g}{s \text{ cm}^3}$ , and  $n_X$  is the stoichiometric coefficient of X. Replacing

for the molar concentrations,

$$q_{X} = -n_{X}k\rho^{a+b} \frac{W_{X}}{W_{A}^{a}W_{B}^{b}} M_{A}^{a}M_{B}^{b}, X = A, B$$
(EQ 12)

**Rate of heat generation.** The reaction heat generated per unit time and unit volume, h(t), is the heat released by one mol of reactant multiplied by the time change of the reactant's molar concentration,

$$h(t) = -Q_F \frac{\mathrm{d}}{\mathrm{d}t} [A]$$
(EQ 13)

where  $Q_F$  is the heat generated by consumption of one mol of species A (negative sign in EQ 14 indicates the reaction is exothermic - remember the comment made earlier about

heat released versus heat of reaction) and h(t) has dimensions  $\frac{J}{s \text{ cm}^3}$ .

$$h(t) = Q_F n_a k \frac{\rho^{a+b}}{W_A^a W_B^b} M_A^a M_B^b$$
(EQ 14)

Since combustion happens both in the chamber and in the volume in the barrel between the breech and the rear end of the projectile, you need conservation equations for both the compression chamber and the breech-to-pellet regions. I will derive the conservation equations for the compression chamber only; you can easily adapt them to the breech-topellet region.

#### 2.2.1 Overall mass conservation

Consider a time-dependent volume V(t) with an exit opening of area  $A_d$ , through which the gas mixture discharges with mass flow rate  $v_d \rho_d$ , as illustrated in Figure 1 (this is a simplified version of Figure 5 in Ref. (1)). For clarity's sake, Figure 1 leaves out some of the details (such as seal cavities and transfer channel) that do not interfere with the derivation.

FIGURE 1. Compression chamber - piston initial position is at t = 0



The compression chamber volume, V(t), changes as the piston, which has area  $A_p$ , advances with velocity  $v_p$ . For the purpose of these derivations it is irrelevant whether V(t) does or doesn't include the volume in the transfer channel - see Ref. (1) for details. The equation for global mass conservation in the compression chamber, neglecting spacial gradients, is

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho V) = -v_d \rho_d A_d \tag{EQ 15}$$

with  $\rho$  the density of the flammable mixture. Except for the discharge area,  $A_d$ , all variables in this equation are time dependent.

Following the discussion in Ref. (1), calculation of the discharge flow rate,  $v_d \rho_d$ , is based on assuming the discharge pressure is known. This allows us to get a mass flow rate under isentropic expansion,  $\dot{m}$ , which can be corrected through a discharge coefficient,  $C_d$ , to account for discharge losses. The gas mixture density follows the ordinary differential equation

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho V) = -C_d \dot{m} A_d \tag{EQ 16}$$

$$V\frac{\mathrm{d}\rho}{\mathrm{d}t} = -C_d \dot{m}A_d - \rho \frac{\mathrm{d}V}{\mathrm{d}t}$$
(EQ 17)

It is fine to carry out the computations assuming the gas constant is not affected by the combustion products; alternatively, you can re-calculate the gas constant as the composition of the gas changes.

#### **2.2.2 Species conservation**

The mass flow rate of species *X*, where *X* stands for either *A* or *B*, that leaves the chamber per unit area and unit time, is

$$v_d \rho_X = v_d \rho \cdot \frac{\rho_X}{\rho} = C_d \dot{m} M_X$$
 (EQ 18)

The rate at which the species within volume V changes equals the rate at which the species is created inside V, minus the rate at which the species escapes from V (when adapting this equation to the region between the breech and the pellet, the sign of the term containing  $\dot{m}$  switches from negative to positive).

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho_X V) = -C_d \dot{m} A_d M_X + q_X V \tag{EQ 19}$$

$$V\rho \frac{\mathrm{d}M_X}{\mathrm{d}t} + M_X V \frac{\mathrm{d}\rho}{\mathrm{d}t} = -\left(C_d \dot{m}A_d + \rho \frac{\mathrm{d}V}{\mathrm{d}t}\right) M_X + q_X V \tag{EQ 20}$$

Replacing  $V \frac{d\rho}{dt}$  from EQ. 17 and after a little algebra, the species conservation equation reduces to

$$\frac{\mathrm{d}M_X}{\mathrm{d}t} = \frac{q_X}{\rho} \tag{EQ 21}$$

It may seem odd that the mass fraction doesn't depend explicitly on the rate of change of the volume where the reaction takes place (it depends implicitly, however, through the density and the temperature - the latter entering in the function k), but this is a result of the quasi-steady and uniformity assumptions. Replacing for  $q_X$  gives us the following ODEs for species A and B

$$\frac{\mathrm{d}M_A}{\mathrm{d}t} = -n_a k \frac{\rho^{a+b-1}}{W_A^{a-1} W_B^b} M_A^a M_B^b \tag{EQ 22}$$

$$\frac{dM_B}{dt} = -n_a k \frac{\rho^{a+b-1}}{W_A^a W_B^{b-1}} M_A^a M_B^b$$
(EQ 23)

Notice that these two equations do not depend explicitly on the derivatives of the compression chamber thermodynamic variables; this facilitates implementation of the numerical integration.

#### 2.2.3 Energy conservation

It is straightforward to modify the energy equation derived in Ref. (1) by adding the heat of combustion within the chamber - this will be the heat released per unit volume, h(t), multiplied by the chamber volume.

$$\frac{\mathrm{d}}{\mathrm{d}t}[V\rho c_{v}T] = A_{p}pv_{p} - C_{d}\dot{m}A_{d}\left(\frac{1}{2}v_{d}^{2} + c_{p}T_{d}\right) - \frac{\mathrm{d}Q}{\mathrm{d}t} + Vh(t)$$
(EQ 24)

Here,  $\frac{dQ}{dt}$  is the rate of heat outflow through the chamber walls. Expanding this equation, replacing  $V\frac{d\rho}{dt}$  from EQ 17, and after a little algebra, you get an ODE for the chamber temperature

$$V\rho c_{v}\frac{\mathrm{d}T}{\mathrm{d}t} = A_{p}pv_{p} - C_{d}\dot{m}A_{d}\left(\frac{1}{2}v_{d}^{2} + c_{p}T_{d} - c_{v}T\right) - \frac{\mathrm{d}Q}{\mathrm{d}t} + Vh(t)$$
(EQ 25)

#### 2.2.4 Conservation equations summary

The following set of four ODEs describe the thermodynamic state of the compression chamber in the presence of a combustion reaction  $n_aA + n_bB \rightarrow P$ 

$$V\frac{\mathrm{d}\rho}{\mathrm{d}t} = -C_d \dot{m}A_d - \rho \frac{\mathrm{d}V}{\mathrm{d}t}$$
(EQ 26)

$$\frac{dM_A}{dt} = -n_a k \frac{\rho^{a+b-1}}{W_A^{a-1} W_B^b} M_A^a M_B^b$$
(EQ 27)

$$\frac{\mathrm{d}M_B}{\mathrm{d}t} = -n_a k \frac{\rho^{a+b-1}}{W_A^a W_B^{b-1}} M_A^a M_B^b \tag{EQ 28}$$

$$V\rho c_{v}\frac{\mathrm{d}T}{\mathrm{d}t} = A_{p}pv_{p} - C_{d}\dot{m}A_{d}\left(\frac{1}{2}v_{d}^{2} + c_{p}T_{d} - c_{v}T\right) - \frac{\mathrm{d}Q}{\mathrm{d}t} + Vh(t)$$
(EQ 29)

A similar set, with minor changes, applies to the region between the breech and the pellet. These equations must be supplemented with a state equation, and then combined with the spring equations as described in Ref. (1). If you develop your computer code in a modular and organized manner, this modifications are very easy to implement.

#### 2.2.5 Initial molar and mass fraction values

Given an initial temperature and pressure in the compression chamber (usually ambient values), the initial amount of proxy hydrocarbon (and the corresponding mass fractions), must be such that the heat of combustion of the proxy hydrocarbon matches the heat released by a known amount of lubricating oil.

It is convenient to do the analysis for a general  $C_m H_n$  hydrocarbon and then particularize the results for our choice of proxy fuel. The reaction of interest is

$$n_F C_n H_m + n_A (\eta O_2 + (1 - \eta) N_2) + n_E (\eta O_2 + (1 - \eta) N_2) \rightarrow P$$
 (EQ 30)

where *P* stands for combustion products, where all the carbon in  $C_n H_m$  goes into  $CO_2$  and all the hydrogen goes into water. This is a global reaction that replaces the complex set of reactions that determine the true chemical path.

Assume  $n_F$  moles of  $C_n H_m$  react with oxygen in an excess amount of air. Denote by  $n_A$  the moles of air required to supply the oxygen needed for stoichiometric balance. Assume the gas mixture contains  $n_E$  moles of additional air. Also assume one mol of air is made up of  $\eta$  moles of molecular oxygen and  $1 - \eta$  moles of molecular nitrogen, where  $\eta = 0.21$ .

Denote by  $Q_L$  the heat generated by burning one gram of lubricant, and remember that  $Q_F$  is the heat generated by burning one mol of  $C_n H_m$ . The number of  $C_n H_m$  moles you need to match the energy of q mg of lubricant<sup>1</sup> is

$$n_F = q \, 10^{-3} \frac{Q_L}{Q_F} \tag{EQ 31}$$

Since to burn one mol of  $C_n H_m$  you need n + m/4 moles of  $O_2$ , the number of air moles for stoichiometric combustion is

$$n_A = \frac{n+0.25m}{\eta} n_F \tag{EQ 32}$$

and number of stoichiometric  $O_2$  moles is

$$n_{O_2} = n_F (n + 0.25m) \tag{EQ 33}$$

To get  $n_E$ , consider the total number of moles in the reaction,  $n_T = n_F + n_A + n_E$ 

<sup>1.</sup> Milligrams is a convenient and intuitive unit of measure for burnt oil.

and use the proportionality  $\frac{1 \text{ mol}}{V^* \text{ cm}^3} = \frac{n_T \text{ mol}}{V \text{ cm}^3}$ , where  $V^*$  is the volume occupied by one

mol of ideal gas (about 24, 400 cm<sup>3</sup> at 1 atm and 25 C), and V is the initial volume of the compression chamber (initially the only volume that matters is the compression chamber since the pellet can be assumed to be in the plane of the breech). Since  $n_T = \frac{V}{V^*}$ , the number of males of extra air is

ber of moles of extra air is

$$n_E = \frac{V}{V^*} - (n_F + n_A)$$
(EQ 34)

Replacing for  $n_A$ 

$$n_E = \frac{V}{V^*} - n_F \left( 1 + \frac{n + 0.25m}{\eta} \right)$$
(EQ 35)

The initial density of the gas mixture,  $\rho_0 = \rho(0)$ , is

$$\rho_0 = \frac{n_F W_{C_n H_m} + (n_A + n_E) W_{AIR}}{V}$$
(EQ 36)

where  $W_{AIR}$  is the molecular weight of the air. Alternatively,

$$\rho_0 = \frac{W_{AIR}}{V^*} + q 10^{-3} \frac{Q_L}{Q_F} \frac{W_{C_n H_m} - W_{AIR}}{V}$$
(EQ 37)

where the first term on the right is the density of the gas in the absence of fuel, and the second term is a correction for the presence of fuel. Notice the orders of magnitude in the second term on the right. The number of milligrams of lubricating oil, q, is of order one. The initial volume of the chamber, V, is about 50 cm<sup>3</sup>. The ratio  $Q_L/Q_F$ , as we will see shortly, if about 0.02. This means the second term is several orders of magnitude smaller than the first. Therefore, we can safely compute the starting global density ignoring the fuel component.

The initial fuel mas fraction is

$$M_{C_n H_m} = \frac{\rho_{C_n H_m}}{\rho_0} = \frac{n_F W_{C_n H_m}}{V \rho_0} = q 10^{-3} \frac{Q_L}{Q_F} \frac{W_{C_n H_m}}{V \rho_0}$$
(EQ 38)

The denominator on the right side of this equation is a weak function of q, which means that to first order the fuel mass fraction is a linear function of the number of milligrams of lubricant in the chamber.

The initial oxygen gas mass fraction is,

$$M_{O_2} = q 10^{-3} (n + 0.25m) \frac{Q_L}{Q_F} \frac{W_{O_2}}{V \rho_0}$$
(EQ 39)

which to first order is also a linear function of q.

#### **2.3** Single-step n-octane reaction

A stoichiometrically-balanced global n-octane reaction with oxygen gas is as follows,

$$C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O$$
 (EQ 40)

There are several single-step formulations for n-octane combustion. We will use the single-step model proposed by Westbrook (Ref. 3),

$$\frac{d}{dt}[C_3H_8] = -k[C_3H_8]^a[O_2]^b$$
(EQ 41)

$$\frac{\mathrm{d}}{\mathrm{d}t}[O_2] = -12.5k[C_3H_8]^a[O_2]^b$$
(EQ 42)

with partial reaction orders a = 0.25 and b = 1.5, and

$$k = F \exp\left(\frac{-T_a}{T}\right) \tag{EQ 43}$$

where  $T_a = 20,000$  K and  $F = 7.2 \times 10^{12} \frac{\text{cm}^{2.25}}{\text{s mol}^{0.75}}$ .

#### 2.3.1 Initial values for n-octane

Assume the heat released by burning one gram of lubricating oil to be 42,000 J and the heat released by burning one mol of n-octane to be 5,144,000 J. This value is lower than you find in heat of reaction tables because it is calculated from bond braking and formation only, and does not include the heat of water condensation. This is justified since the energy balance in our air gun precludes the transfer of water condensation energy to the pellet kinetic energy.

$$Q_L = 42 \times 10^3 \frac{\mathrm{J}}{\mathrm{g}} \tag{EQ 44}$$

$$Q_F = 5.144 \times 10^6 \frac{\mathrm{J}}{\mathrm{mol}}$$
(EQ 45)

To match the energy released by q mg of lubricating oil, we need the following number of moles of n-octane,

$$n_F = q 10^{-3} \frac{Q_L}{Q_F} \text{mol}$$
(EQ 46)

The following table shows the initial values for one mg lubricant oil.

**TABLE 1.** Starting values  $V = 50 \text{ cm}^3$ , T = 298.15 K, p = 101.325 kP,  $V^* = 24,400 \text{ cm}^3$ , 1 mg chamber oil

C <sub>8</sub> H <sub>18</sub> moles	Air moles	Extra air moles	O <sub>2</sub> moles	Gas density (g/cm3)	C <sub>8</sub> H <sub>18</sub> mass fraction	O <sub>2</sub> mass fraction
8.165E-06	4.860E-04	1.555E-03	4.286E-04	1.196E-03	1.557E-02	2.294E-01

**Equivalence ratio.** The equivalence molar ratio tells you how lean or rich the fuel/air mixture is.

$$\phi = \frac{\left[\frac{n_F}{n_A + n_E}\right]}{\left[\frac{n_F}{n_A}\right]_{\text{stoichiometric}}}$$
(EQ 47)

Figure 2 shows the n-octane/air equivalence ratio for a compression chamber with volume 50 cm<sup>3</sup>. Full combustion with no excess air occurs with approximately 4.15 mg of lubricating oil; this corresponds to about 83 mg of oil per liter.

FIGURE 2. N-octane/air equivalence ratio at one atm and 25 C - chamber volume 50 cm3



## 3.0 Results and discussion

The computations refer to the Beeman RS2 gun specified in the Table 2, taken from Ref. (1), firing JSB 4.5 mm pellet with weight 0.670 g (10.34 gr) at a nominal muzzle velocity of 247.5 m/s (812 ft/s). The nominal velocity, measured without new lubrication, is a reference velocity used to calibrate the internal ballistics model parameters, as discussed in Ref. (1). This doesn't mean the nominal velocity is free from dieseling effects. I make the implicit assumption that whatever dieseling effects exist without new lubrication are small and superimpose linearly to additional dieseling effect presented in the results<sup>1</sup>.

Spring			Piston			Chamber		
Free length	285.75	mm	Weight	0.298	Kg	Diameter	25	mm
Number coils	43		Piston head thickness	12	mm	Seal cavity comp. depth	0.53	mm
Outside diameter	17.78	mm	Seal thickness	6.7	mm	Transfer port diameter	3.4	mm
Wire diameter	3.02	mm				Transfer port length	23	mm
Spring precompression	52.705	mm						
Rear spacer thickness	0	mm						
Front spacer thickness	7.49	mm						
Cocking stroke	100	mm						
Guide length	100	mm						

TABLE 2. Beeman RS2 air rifle specifications - taken from Ref. (1)

The results and conclusions that follow are for adiabatic conditions at standard atmospheric initial state (101.135 kPa pressure and 25 C temperature) and calibrated model parameters as discussed in Ref. (1). It is important to keep in mind that the detailed picture of events that follows is conditional on the assumptions of the approach. These calculations are meant to be descriptive and conceptual rather than predictive.

**Sequence of events.** The diagrams in Figure 3 show the position of the piston and pellet at four critical times, from the start of the firing cycle to the moment the pellet exits the muzzle, from top to bottom. Although the diagrams are not to scale, they clearly show that the combustion flash happens before the pellet has had a chance to move more than a few millimeters into the barrel. The tiny space the pellet clears away from the breech when autoignition starts contains flammable fuel - this fraction of fuel causes the dieseling event to occur, in small part, outside the compression chamber and past the breech. Because the drawings are not to scale, this fraction is actually smaller than the diagram in Figure 3 suggests. For practical purposes we can assume the dieseling event ends before the pellet moves. The duration of the dieseling flash itself is irrelevant - it happens too fast to be detectable though the piston displacement.

Figure 4 illustrates the impact dieseling has on the piston position at the time the pellet leaves the muzzle. Combustion causes the piston to recede further back, creating a larger volume in the chamber where hot air remains as the pellet leaves. Not only is the energy associated with this hot air lost, but the spring deflection is higher, causing additional energy to be retained by the spring, some in the form of vibrational motion.

<sup>1.</sup> The nominal values in this report differ slightly from those in Ref. (1) due to different atmospheric values.

FIGURE 3. Piston and pellet positions at four critical times - dieseling event of 2 mg oil (Beeman RS2 rifle, JSB 4.5 mm 670 g pellets).



FIGURE 4. Terminal piston positions with and without dieseling (2 mg oil burnt).



The combustion event. An important feature of ignition at high temperatures is that it happens extremely quickly. In the competition between the pre-exponential factor, which represents the likelihood that molecules will collide in the right manner as to react with one another, and the activation temperature (or energy), which affects the probability that the colliding molecules will have enough energy to break the bonds needed for the reaction to take place, eventually the exponential temperature component takes over and the reaction proceeds extremely fast.

Figure 5 clearly shows the extremely fast completion of the combustion reaction once the exponential temperature component of the Arrhenius equation takes over. The figure shows that shows the evolution of the  $C_8H_{18}$  mass fraction as a function of time on the left vertical axis, and the piston velocity on the right vertical axis.

The mass fraction curve *looks* like a step function, dropping to zero at a time slightly above 9 ms. This is not a step function, however, but a function that very quickly begins to drop at about 9 ms, the time when the activation temperature overwhelms the pre-exponential factor.

What Figure 5 also illustrates is the very different time scales associated with the chemistry vis-a-vis the movement of mechanical components. The chemistry time scale is of the order of the time interval where the mass fraction drops from an almost constant value to essentially zero. The mechanical components time scale, on the other hand, is given by the entire firing cycle, namely about 10 ms. This difference in time scales is evidence of the stiffness property of differential equations when chemical reactions are involved - something you must keep in mind when programming the numerical solution of your ODE system. *The dieseling event is essentially complete in less than three hundredths of a millisecond*, a time scale far shorter than anything else involved in the firing cycle.





Notice the sign change in the piston velocity - this is the time the piston bounces and starts moving backwards. This is in agreement with the diagrams in Figure 3, where ignition precedes the bounce by 0.5 ms.

**Dieseling energy and pellet energy.** Figure 6 shows the projectile energy gain, in Joules, for varying amounts of oil burnt. The plot shows three regimes, indicated by breaks in the line slope. The first break, which occurs at about 0.25 mg oil burnt, is related to the bouncing of the piston at the end of its stroke. For this particular gun and choice of pellet, calculations show that in the absence of dieseling the piston hits the end of the chamber before bouncing. In the second regime, dieseling changes this picture. Computations show that combustion of 0.25 mg of oil or greater causes the piston to bounce before hitting the end of the chamber. Intuitively, this makes sense, since the sudden flash of oil burning forms a gas pillow that cushions the piston at the end of its forward travel.

The second break in the line corresponds to the stoichiometric balance of the proxy fuelair mixture, which, as Figure 2 shows, corresponds to slightly more than 4 mg of lubricant. If the amount of fuel is greater than its stoichiometric value, the oxygen in the air will run out before the full amount of fuel burns, and only part of the lubricant energy will be released, the rest being expelled with unburned fuel out of the muzzle. Again, keep in mind that the details of this picture hinge on the assumption of this simple model.

Between these two breaks, power gain is a linear function of burnt oil. Under the conditions of this model, the Mach number at the transfer port remains subsonic for all amounts of oil. The reason for this is that as the oil consumed in combustion increases, the temperature at the transfer port rises, keeping the speed of sound large enough to limit the rise of the Mach number.





Figure 7 shows the muzzle velocity for the 4.5 mm JSB 10.34 gr pellet. In the absence of combustion, the muzzle velocity is 247.5 m/s (812 ft/sec). This figure suggests supersonic shots occur when slightly over 3 mg of oil is consumed in dieseling. Three milligrams is approximately half drop of oil (depending on you means of dispensing the oil, obviously). Qualitatively, this what we observe - one drop of oil injected directly into the compression chamber through the transfer port may produce at least one supersonic shot.

FIGURE 7. Pellet velocity - (Beeman RS2 rifle, JSB 4.5 mm 670 g pellets).



Figure 8 shows the fraction of burnt lubricating oil energy that gets converted into muzzle energy - I refer to this fraction as *combustion efficiency*. For small amounts of oil (less than 0.25 mg), this fraction is about 30%, for moderate and large amounts (over 1 mg), this value drops to about 15%. For amounts of oil beyond equivalence ratio one, efficiency drops monotonically as increasing amounts of oil fail to burn. There is an interesting message behind these values. *For very small amounts of oil involved in dieseling, the efficiency of the oil to deliver power to the projectile is comparable to the efficiency of the main spring, for large amounts of oil, the efficiency of dieseling oil can be significantly lower than the spring's. This is an important conclusion for anyone considering using dieseling as a means to enhance a gun's muzzle energy.* 





**Dieseling impact on temperature.** Figure 9 shows the peak temperature in the chamber as a function of the amount of oil burnt. This picture makes intuitive sense, with temperature rising linearly as a function of the amount of oil involved in dieseling, and then leveling off when the oil exceeds the stoichiometric balance. These can be very considerable temperatures, something that shouldn't come as a surprise to air gun enthusiasts when they find burnt seals.

**Dieseling impact on pressure.** What happens to the pressure is much less obvious than what happens to the temperature and deserves some elaboration. Intuition might tell you that the sudden release of thermal energy in a confined space must result in a higher pressure. There are two issues here. First, we must clarify what we mean by "confined" - in the case of a spring-piston air gun, the chamber volume is not confined in the same way the volume inside an internal combustion engine cylinder is confined. Our compression chamber has a movable surface (the piston seal) which is connected to a spring, and is therefore not rigidly connected to a moving part, as is the case with the internal combustion engine piston. This is important because depending on the timing of the ignition, the piston in the air gun may be able to absorb more or less of the energy from dieseling.





The other issue is thermodynamic in nature. Dieseling injects enthalpy into the compression chamber, and pressure is only one component of enthalpy. The combined effect of a flexible wall in the chamber (the front end of the piston seal) with the ability of the gas to alter its energy content through a change in both temperature *and* pressure means that you can have almost no change or even a drop of peak pressure as a result of dieseling! If instead of n-octane we use propane ( $C_3H_8$ ) as a proxy fuel, this is precisely what we find.

This is easier to visualize if you consider that what matters is not only how high the pressure is, but how *long it acts* on the projectile. The combustion flash causes the piston to bounce earlier, creating a larger volume of high temperature air in the chamber than would be the case without combustion. This additional volume of air provides a more sustained push to the pellet than would be the case without combustion. A more sustained push may accelerate the pellet to higher velocity, even if the push occurs at lower pressure.

Figure 10 illustrates how different the pressure history can be depending on the proxy fuel we use. Burning propane as proxy fuel has a much smaller impact on peak pressures than burning n-octane, even though in both cases the amount of energy injected through combustion is exactly the same.

There is no rigorous scientific evidence of what happens to the pressure within a dieseling air gun. Cardew and Cardew (Ref.(5)) claim to have measured significant increases in peak pressure as result of dieseling. Unfortunately, they are not able to quantify how large this peak was because, as quoted in their book, their instrumentation failed as a result of the pressure spike. Nevertheless, accepting that dieseling causes the pressure in the compression chamber to go up, we must conclude that n-octane gives us a better model than propane for what really happens.

Peak pressure heights are associated with both the pre-exponential factor and the activation energy of the fuel. The fact that n-octane has higher pre-exponential factors and, in the model used here, also higher activation temperature than propane explains the difference in peak pressures. FIGURE 10. Pressure history in the compression chamber for 1 mg lubricating oil burnt - (A) computed with n-octane, and (B) obtained with propane as proxy fuel. In both cases, ignition happens very close to 9 ms, and in both cases pellet velocity gains differ by less than 3 m/s.



Figure 11 shows the peak pressures as function of oil involved in dieseling using n-octane as a proxy fuel. The highest peak pressure occurs for a stoichiometrically balanced mix-ture.

FIGURE 11. Chamber peak pressure - (Beeman RS2 rifle, JSB 4.5 mm 670 g pellets).



**Impact of dieseling on energy balance.** Why is it that only a fraction of the energy released through lubricant combustion gets communicated to the projectile? The dieseling event causes a complicated redistribution of energy among the spring, the piston, and the compression chamber volume at the time the pellet exits the muzzle. The following two panels illustrate this with numbers.

Notice the places where the dieseling energy goes. Of the 42 J of energy that 1 mg of oil releases into the compression chamber, slightly under 8.5 J go to the pellet, the rest gets distributed among the various internal components, roughly as follows.

- 1. The main spring retains almost 4 J of extra deflection energy this is because dieseling causes a more pronounced bounce.
- 2. The main spring also increases its kinetic energy from about 2 J to almost 3.3 J some of this energy translates into greater spring vibration.
- 3. The piston gains about 5.25 extra Joules of energy this is because of the more pronounced bounce.
- 4. The compression chamber, which in the absence of dieseling ends up with an energy *deficit* of over 3 J, now reaches the end state with an energy *surplus* of over 8.75 J this is the combined impact of a more violent bounce and hotter air after the dieseling flash.
- 5. As a result of dieseling, the air behind the pellet as the pellet leaves the muzzle is hotter and it retains about 6 J of extra energy - this energy will leave the barrel after the pellet exits and is therefore wasted.
- 6. Notice also that the pellet loses about five additional Joules to friction as a result of dieseling this may sound counterintuitive, but it is precisely what you would expect. Remember that friction comes both from the pellet nose and the pellet skirt, and that skirt friction is a function of the pressure behind the pellet (see Ref. (1) for details). Dieseling sustains high pressure behind the pellet over a longer segment of the pellet travel within the bore, and as a result, more energy gets wasted.
- 7. Finally, notice the 42.02 J at the bottom of the panel in Table 4 this is the net energy introduced into the system by one mg of lubricant, and is also a form of reassurance that the calculations are correct, since energy must be conserved (the exact figure should be 42.00 J the 0.02 difference is due to numerical truncation error in the integration of the ordinary differential equations).

Energy Balance (J) - No dieseling					
Area	Energy	Start	Finish	Diff	Fraction
	Elastic	71.79	16.09	-55.70	-77.6%
	Kinetic	0.00	1.97	1.97	2.7%
Spring	Guide	0.00	0.00	0.00	0.0%
	Total	71.79	18.05	-53.74	-74.9%
	Kinetic	0.00	4.50	4.50	6.3%
	Impact	0.00	6.65	6.65	9.3%
Piston	Friction	0.00	2.17	2.17	3.0%
	Outflow	0.00	-4.59	-4.59	-6.4%
	Total	0.00	8.74	8.74	12.2%
	Thermal	12.50	8.85	-3.65	-5.1%
Chambar	Transfer	0.05	0.45	0.40	0.6%
Chamber	Heat loss	0.00	0.00	0.00	0.0%
	Total	12.55	9.30	-3.25	-4.5%
	Thermal	0.00	13.99	13.99	19.5%
Breech to	Kinetic	0.00	0.13	0.13	0.2%
pellet	Heat loss	0.00	0.00	0.00	0.0%
	Total	0.00	14.12	14.12	19.7%
Mussle	Outflow	0.00	0.84	0.84	1.2%
wuzzie	Total	0.00	0.84	0.84	1.2%
Pellet	Linear KE	0.00	20.51	20.51	28.6%
	Rot KE	0.00	0.01	0.01	0.0%
	Friction	0.00	12.78	12.78	17.8%
	Total	0.00	33.30	33.30	46.4%
		0.00	0.0%		

TABLE 3. Energy balance without dieseling - nominal configuration with JSB 0.670 g pellets

 TABLE 4. Energy balance - 1 mg dieseling lubricant and JSB 0.670 g pellets.

Energy Balance (J) - 1 mg oil dieseling					
Area	Energy	Start	Finish	Diff	Fraction
Gardina	Elastic	71.79	20.28	-51.52	-71.8%
	Kinetic	0.00	3.30	3.30	4.6%
Spring	Guide	0.00	0.00	0.00	0.0%
	Total	71.79	23.58	-48.21	-67.2%
	Kinetic	0.00	16.09	16.09	22.4%
	Impact	0.00	0.00	0.00	0.0%
Piston	Friction	0.00	2.24	2.24	3.1%
	Outflow	0.00	-4.32	-4.32	-6.0%
	Total	0.00	14.00	14.00	19.5%
	Thermal	12.63	20.81	8.18	11.4%
Chambar	Transfer	0.05	0.65	0.60	0.8%
Champer	Heat loss	0.00	0.00	0.00	0.0%
	Total	12.69	21.46	8.77	12.2%
	Thermal	0.00	20.12	20.12	28.0%
Breech to	Kinetic	0.00	0.18	0.18	0.3%
pellet	Heat loss	0.00	0.00	0.00	0.0%
	Total	0.00	20.30	20.30	28.3%
Mumle	Outflow	0.00	0.91	0.91	1.3%
iviuzzie	Total	0.00	0.91	0.91	1.3%
	Linear KE	0.00	28.92	28.92	40.3%
	Rot KE	0.00	0.02	0.02	0.0%
Pellet	Friction	0.00	17.31	17.31	24.1%
	Total	0.00	46.25	46.25	64.4%
		42.02	58.5%		

## 4.0 Concluding remarks

A conceptual treatment of combustion within the compression chamber of a spring-piston air gun can be carried out with limited resources by making significant assumptions about the physics involved, while retaining the most important aspects of the phenomenon. Those assumptions are that the combustion process can be modeled with a proxy fuel whose chemistry is well documented, that space gradients and diffusion are not important, and that the kinetic energy component of the gas in the compression chamber is negligible when compared with the thermal energy.

*Under these assumptions*, this analysis tells us some interesting things: a) between 30% and 15% of the lubricant energy translates into additional projectile kinetic energy, b) the combustion process is essentially over before the pellet has had a chance to move significantly into the bore, and c) over 70% the energy released by the combustion gets absorbed by the internal mechanical components (higher spring deflection/vibration), as well as by heat trapped in the chamber and behind the pellet by the time the pellet leaves the barrel.

Finally, it is important to keep in mind that this was a conceptual, not a predictive analysis. The results reported here must be viewed with caution until a more comprehensive numerical study and experimental verification become available. A full solution to the dieseling problem requires the numerical solution of the reactive compressible Navier-Stokes equations, which you can expect would yield results that differ somewhat from what I discussed here. If and when the time of such an undertaking comes, I hope these observations will serve as a useful research guide.

## 5.0 References

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