CLOSED VESSEL EXPERIMENT MODELLING AND BALLISTIC PARAMETER ESTIMATION OF GUN PROPELLANTS FOR LIFETIME PREDICTION

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Abstract — **A closed vessel is an apparatus with very thick walls, in which propellants under test are burnt. After ignition, gaseous products and heat are produced. The time history of pressures is measured by piezoelectric transducers, and recorded in either an analog or digital way. For the design and simulation of a gun performance, it would be rather important if one could use the thousands of P versus t points generated by a single shot for the estimation of as many as possible ballistic parameters. The present work is devoted to the development of predictive models for the closed vessel, comparing the performance to real experimental data. Using known regression procedures (Maximum Likelihood, for instance), ballistic parameters are fitted and lifetime of the propellant can be predicted. This can be done once such parameters are related to its ageing process, which consists of a loss of volatile components.**

Keywords — **Closed vessel, propellant and ageing.**

1. INTRODUCTION

A closed vessel is a robust pressure vessel used for propellant testing. The propellant is placed in the vessel, which is then sealed, and ignition is remotely commanded by a computer that, after ignition, also acquires pressure versus time data. Such ignition is promoted by an electric current on a filament that ignites a small amount of primer (in general, black gunpowder). Devices named squibs, stronger than electric pyrotechnic fuses, are also used for this purpose. Fig. 1 (extracted from the equipment manual) shows the exploded view of a closed vessel.

The modern trend to turn ordnance lighter and more efficient without decreasing reliability leads to a search for greater knowledge of the phenomena involved in propellant burning; in barrel / tube guns this involves estimating the actual ballistic parameters of the propellant in use.

Some of these parameters can be evaluated through thermochemical calculations as in the well-known Hirschfelder-Sherman method (1942, 1943). However, this approach has the disadvantage of requiring an accurate chemical description of the propellant, rather than using experimental data on pressure profiles to improve its quality. Ageing of the propellant continuously changes its composition, through irreversible auto-catalytic reactions in which volatile compounds are formed and evolve from propellant grains. Ageing is accelerated by humidity, by stockpiling temperature and by the loss of stabilizers. These facts reduce the mechanical integrity of propellant grains, producing pressure picks that are critical for safety of ammunition, rocket engines, cannons, mortars, etc... Therefore, in order to decide whether an aged propellant can still be used, it would be necessary to evaluate its actual chemical composition (by High Efficiency Liquid Chromatography, for instance), calculate its ballistic parameters through Hirschfelder-Sherman methods and use a gun simulation algorithm to predict the projectile muzzle velocity. Unfortunately, no analytical procedure is consolidated to elucidate propellant chemical composition and the approach is not used; instead, a heuristic criterion is traditionally employed.

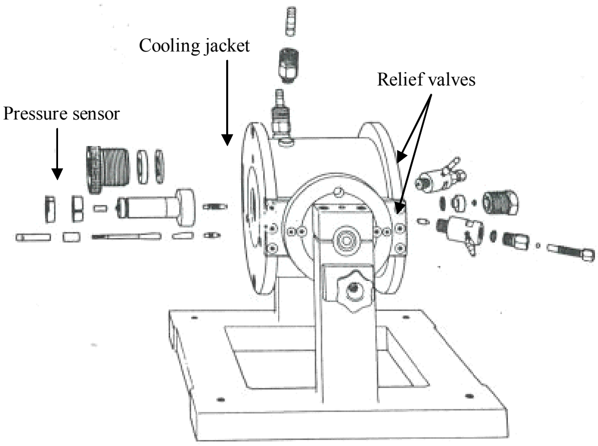

Fig. 1. Exploded view of a closed vessel

The present work is devoted to the development of material balances inside closed vessels. These balances are coupled with empirical burn rate expressions and the model built this way has its performance compared to experimental data, using known regression procedures (Maximum Likelihood, in this case). The necessary experimental data is provided by typical closed vessel experiments, in which the propellant used was artificially aged by a heating protocol.

2. METHODS

A. Ageing Method

Propellants of conventional weapons exhibit the phenomenon of nitrocellulose (NC) decomposition. According to Klerk and van Driel (2002), this decomposition affects the mechanical integrity of propellants affecting their combustion during a typical ballistic cycle. These authors observed, using GPC, that polymeric chains of NC seem to be broken in both naturally and artificially aged propellants, resulting in unacceptable pressure picks inside weapons, especially for large load densities. This transformation increases the superficial area of propellant grains by fractures in their surface as well as by a porosity decrease that accelerates burning rates and contributes to the occurrence of pressure picks. Additionally, in double base propellants, nitrogen oxides evolve from the grain, react with atmospheric humidity and the acids thus formed (HNO_3) attack plasticizers and stabilizers (carbamite), turning the decomposition into a sort of auto-catalytic process:

$$NO_x + x/2\ H_2O + 3x/4\ O_2 \leftrightarrow xHNO_3 \qquad (1)$$

To simulate this, Judge (2003) tested several ageing protocols and considered that the oxidation and the migration of the plasticizers are related to molecular reactions or diffusion effects governed by kinetic relationships that are accelerated by heating. Additionally, the author states that plasticizers loss by evaporation in non-confined propellants causes greater degradation of mechanical properties than in confined ones; therefore, propellants should be stored confined and without contact with oxygen in a stamped packing.

For the propellant used in this work, preparation (comminution, for instance) was not necessary, because it was already present in a granular form. Samples were weighted according to the desired load densities (0.08, 0.09 and 0.10g/cm3) and sealed in resistant glass pots, following the Stanag 4527 (2000) and 4117 (2001) standards. According to these standards, an artificial ageing protocol consisting of 120 days in a controlled temperature of 65.5°C corresponds to a 10-year storage time at a typical storeroom. Once the gunpowder lot used in this study was manufactured in 2002, a 60-day heating protocol was preferred for safety reasons and would correspond to a 5-year period of storage. This artificial ageing was carried out in an oven capable of maintaining a fixed temperature and equipped with internal recirculation not only to exhaust generated gases but also to maintain humidity conditions and eliminate temperature gradients. Following the same standards, the pots were not completely filled with propellant (a clearance space was left) and were loosely closed on purpose, for safety reasons. This last procedure might seem to interfere on experimental reproducibility. However, only when the propellant looses its ballistic reproducibility, its burning behavior begins to depend on sealing conditions and, consequently on the chemical composition of the gaseous atmosphere inside the pot (because of the undesirable auto-catalytic reactions); and that is exactly what we are trying to detect.

Three pots, corresponding to the three chosen load densities, were removed from the oven at each of the 8 weeks up to a total of 24 shots in the closed vessel. Therefore, a shot was performed for each load density, because as will be seen, modelling requires 3 shots with different load densities to estimate ballistic parameters. In this procedure, metallic plates were placed near the oven for the discharge of static electricity - nearly 1000g of gunpowder was in the oven.

B. Mathematical Modelling, Numerical Simulation and Parameter Regression

The model is based on the following hypotheses:

a) there is no heat loss from the system to the environment, because the burning time is very small compared to the typical dynamics of heat transfer processes.

b) inside the vessel, there is a decomposition reaction given by Solid (s) → Gas (g).

Hypothesis b indicates that it is not possible (or not of interest) to predict the chemical composition of generated gaseous mixture but only its lumped thermochemical behavior as well as its kinetics of formation.

According to Piobert (1839), the burning of a propellant, once is a surface phenomenon, takes place in parallel layers. Therefore, it is convenient to define a characteristic dimension of the grain as the smallest distance between two opposite burning surfaces that has to be burnt through for complete combustion of the propellant grain. This characteristic dimension is called web size of the grain (in meters and usually denoted by D). Thus, a propellant shaped in thin stripes (in which the thickness is too small when compared to both width and length – the lateral burning area can therefore be neglected), the web is the thickness itself; in a long cylinder, it is the diameter; in a tube, it is the wall thickness.

The fraction of the web remaining after a time t (in seconds) of combustion is given by:

$$f(t) = \frac{D(t)}{D_0} \qquad (2)$$

The fraction of volume consumed is:

$$z(t) = \frac{V_0 - Vs(t)}{V_0} \qquad (3)$$

where Vs(t) and V_0 are, respectively, the volume at time t and its initial value.

Henceforth, obvious time-dependencies will be suppressed for the sake of simplicity. The relationship between f and z is known as form function and has a generalized expression given by:

$$z = (1 - f)(1 + \theta f) \qquad (4)$$

where θ is the form factor which depends on grain geometry.

If $\theta > 0$, surface area decreases during burning and the powder is called regressive; if $\theta < 0$, surface area increases during burning and the powder is called progressive; and if $\theta = 0$, surface area remains constant and the powder is called neutral. The propellant employed in this work is presented in ribbons, which have $\theta = 0$; however, this parameter was also included in the list of parameter to be fitted, in order to take into account border effects.

When all the powder is consumed in a closed vessel, i.e., when its mass is completely burnt ($z = 1$ and $f = 0$), pressure assumes its maximum value and begins to decrease, by cooling of the equipment due to external convection - in fact, this is the last P value registered by the computer.

It is reasonable to assume that, at all times, the gas is at the adiabatic flame temperature T0 and Nobel-Abel equation of state is commonly used for the gas, which leads to:

$$P\max(V - nb) = nRT0 \qquad (5)$$

where V is the vessel volume (in m^3), Pmax the pressure after the shot (in Pa), n is the final number of moles of gas generated, R is the universal constant of gases ($R = 8.34$ J/mol.K) and T0, is the adiabatic flame temperature (in K).

The mass of gas generated equals the amount of powder admitted in the vessel, which leads to:

$$P\max\left(V - \frac{ms_0}{\overline{\overline{PM}}}.b\right) = \frac{ms_0}{\overline{\overline{PM}}}RT0 \qquad (6)$$

where ms_0 is the mass of powder used (in g) and $\overline{PM}$ is the average molecular weight of generated gases (in g/mol).

If one divides Eq. (6) by ms_0, it can be found that:

$$\frac{P\max}{\Delta} = \bar{f} + P\max.\eta \qquad (7)$$

where $\Delta = ms_0/V$ is the load density of the experiment (in g/m^3); $\bar{f} = \dfrac{RT0}{\overline{\overline{PM}}}$, is the specific force constant (in J/g) and $\eta = \dfrac{b}{\overline{\overline{PM}}}$ is the specific covolume (in m^3/g). With at least 3 shots, a straight line can be fitted for Pmax/Δ *versus* Pmax and estimatives for η and $\bar{f}$ are found.

With all the thousands of time-dependent data points obtained in an experiment, some dynamic information can also be found. For that, the Vielle/Muraour (Corner, 1950) regression equation can be used, which gives the linear velocity of burning:

$$v = -D_0\frac{df}{dt} = \beta.P^{\alpha} \qquad (8)$$

where β and α are also parameters to be fitted (the last one in $m/s.Pa^{\alpha}$).

Once the rate Eq. (8) is established, it can be assumed that the Nobel-Abel equation of state (Corner, 1950) is valid at all times:

$$P(t)\left[Vg(t) - n(t)b\right] = n(t)RT0 \qquad (9)$$

where P(t), Vg(t) e n(t) are, respectively, the pressure, the volume of gas, and the number of moles of gas at time t with all the values in the same units as before.

Proceeding as before, one can find:

$$P(t)\left[Vg(t) - mg(t)\eta\right] = mg(t)\bar{f} \qquad (10)$$

where mg(t) is the amount of gas at time t.

By the definition of z in Eq. (3) and once the volume and mass are limited by:

$$V = Vs(t) + Vg(t) \text{ and } ms_0 = ms(t) + mg(t) \qquad (11)$$

where Vs(t) and ms(t) are, respectively, the volume and mass of the (solid) propellant on instant t, one can find:

$$Vg(t) = V - \frac{ms_0.(1-z)}{\rho s} \text{ and } mg(t) = ms_0.z \qquad (12)$$

where ρs is density of the propellant.

Equation (12) can be used in Eq. (10) leading to:

$$P\left[V - \frac{ms_0.(1-z)}{\rho s} - ms_0 z\eta\right] = ms_0 z\bar{f} \qquad (13)$$

where:

$$z = \frac{P\left[\dfrac{ms_0}{\rho s} - V\right]}{ms_0\left[P\left(\dfrac{1}{\rho s} - \eta\right) - \bar{f}\right]} \qquad (14)$$

Equation (4) can be solved for f:

$$f = \frac{(\theta-1) \pm \sqrt{(\theta-1)^2 - 4\theta(z-1)}}{2\theta} \qquad (15)$$

Substituting Eq. (14) in (15), one can find:

$$f = \frac{(\theta-1) \pm \sqrt{(\theta-1)^2 - 4\theta\dfrac{K1.P + K3}{K2.P - K3}}}{2\theta} \qquad (16)$$

where $K1 = ms0.\eta - V$, $K2 = ms0(1/\rho s - \eta)$ and $K3 = ms0\,\bar{f}$.

When one differentiates (16) and substitutes the derivative in Eq. (8), a differential equation for P as a function of time is found (for integration with typical methods such as Euler, MILNE, Runge-Kutta, etc):

$$\frac{dP}{dt} = \frac{\beta}{D_0}P^{\alpha}\frac{\left(K2.P - K3\right)^2}{K3\left|K1 + K2\right|} \times \times\sqrt{(\theta-1)^2 - 4\theta\frac{K1.P + K3}{K2.P - K3}} \qquad (17)$$

where the signal of Eq. (16) was conveniently chosen in (17) to make dP/dt always positive (pressure only increases).

For the generation of a theoretical pressure history, a recursive Euler procedure is employed, using the sampling time as the increment Δt and starting with the atmospheric pressure:

$$P(t) = P(t-\Delta t) + \left.\frac{dP}{dt}\right|_{t-\Delta t}\Delta t \qquad (18)$$

It is worth saying that this is performed only for z [given by Eq. (14)] is less that 1; when z reaches this value (all burnt powder), the derivative is substituted by zero and pressure remains constant $\left(P_i^c = P_{i-1}^c\right)$.

For the estimation of α and β, typical maximum likelihood procedures are used with equally weighted residuals, what leads to a least squares expression (Edgar and Himmelblau, 1988):

$$\underset{\{\alpha,\beta\}}{\text{Min}} \sum_i (P_i^t - P_i^e)^2 \qquad (19)$$

where $\underline{P}^t$ is the vector of theoretical pressures generated by Eq. (18) and $\underline{P}^e$ is the vector of experimental pressures. Such (non-linear) optimization is conducted with Newton-based algorithms, with BFGS updates of the Hessian matrix (Edgar and Himmelblau, 1988).

III. RESULTS AND DISCUSSIONS

A 200 cm^3 closed vessel was used and load densities of 0.08, 0.09 and 0.10 g/cm^3 of a typical double base gunpowder were shot. Such propellant is manufactured with nitrocellulose, nitroglycerine and carbamite at President Vargas Industrial Facility (Fábrica Presidente Vargas - FPV) in the form of 2.05 by 2.05 by 0.25 mm ribbons. Information on the detailed chemical composition is both an industrial and military secret.

Figure 2 shows a typical fit of the model (continuous line) to experimental data (dotted line):

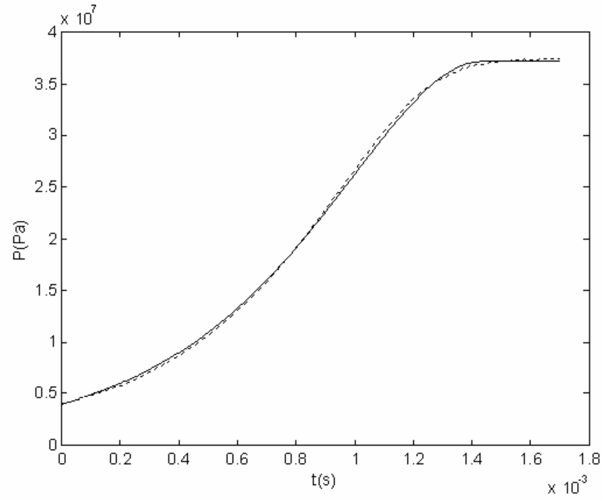

Fig. 2. Typical adherence of the model

Table 1 exhibits the fitted parameters for each load density, at each stage of artificial ageing; Figure 3 depicts the results of Table 1 in a normalized way (the mean values of each entity in each week divided by the maximum value encountered throughout weeks):

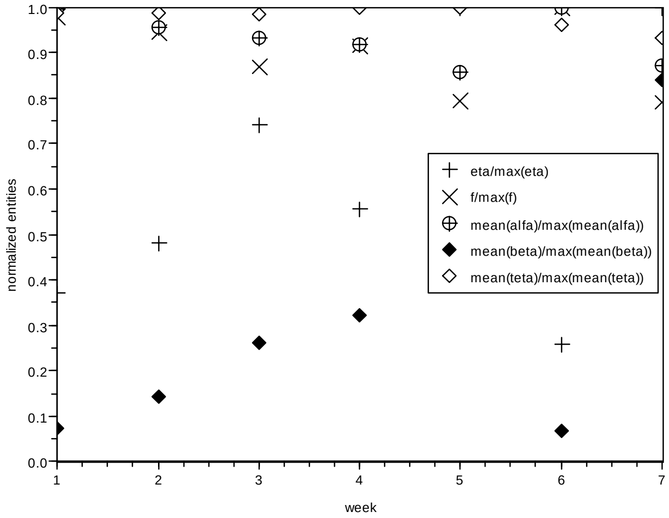

Fig. 3. Normalized values of all entities throughout weeks

Table 1. Values of the fitted parameters

week	η	$\bar{f}$ /10^5	α			β			θ		
			0.08 g/cm^3	0.09 g/cm^3	0.1 g/cm^3	0.08 g/cm^3	0.09 g/cm^3	0.1 g/cm^3	0.08 g/cm^3	0.09 g/cm^3	0.1 g/cm^3
1	0.0010	3.8151	1.1810	1.1349	1.1097	0.0462	0.0881	0.1405	1.0000	1.0863	1.0000
2	0.0013	3.6826	1.1037	1.0981	1.0896	0.1591	0.1864	0.1930	1.0000	1.0000	1.0883
3	0.0020	3.3809	1.0674	1.0364	1.1005	0.3161	0.5016	0.1607	0.9624	1.0122	1.0978
4	0.0015	3.5632	1.0351	1.0641	1.0557	0.5484	0.3019	0.3580	1.0890	1.0000	1.0342
5	0.0027	3.0961	0.9641	1.0022	0.9871	1.6452	0.9457	1.1586	1.1116	1.0128	1.0000
6	0.0007	3.8958	1.1762	1.1254	1.1387	0.0480	0.1122	0.0879	1.0000	1.0000	1.0000
7	0.0027	3.0838	0.9824	1.0289	0.9857	1.3233	0.6133	1.2117	0.9053	1.0123	1.0000

IV. CONCLUSIONS

A model for estimation of the ballistic parameters of propellants was used to elucidate the evolution of such parameters during propellant ageing. For that, an artificial ageing protocol was employed and, at some pre-defined ageing stages, 3 samples were shot with different load densities for regression of 4 ballistic parameters. Two of them (η and $\bar{f}$) were fitted by linear regression [Eq. (7)] and the three other ones (α, β and θ) by nonlinear regression based on dynamic material balances integrated by Euler methods, burning rate empirical formulas and minimum square criteria [Eq. (17) and Eq. (19)]. It must be said that the two fitting procedures were performed in uncoupled and sequential way. As can be seen in Fig. 2, good agreement with experimental data was observed. On Fig. 3, it can be noticed that parameters seem to follow a quite smooth tendency up to weeks 4 and 5, when ballistic reproducibility is completely lost, indicating a limit for ballistic efficiency, in which storage conditions begin to be decisive for ammunition behavior.

Based on the observation of θ values on Table 1, this parameter can be considered unitary and removed from the set of parameters to be estimated for this particular propellant; this could decrease computational time associated to optimization routines.

All this information can be used, along with the fitted parameters, in the simulation of gun performance, preventing overpressures or low muzzle velocities.

Additionally, the adjusted model is useful for the design of new experiments in the closed vessel, for instance, when an increase in load density is needed, based on safety criteria.

For further investigations, some suggestions can be made:

a) more realistic equations of state could be used for gaseous products, such as Peng-Robinson or similar ones;

b) development of a model that would predict gas composition;

c) some sort of correlation between artificial ageing time and the actual one must be established, in order to accurately predict ammunition lifetime;

d) repeated experiments for identical ages, and identical loadings could increase the confidence in parameters values; this was not performed in this study only for safety reasons (to minimize the number of shots).

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