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Research paper

Evaluation of the Burning Rate of Black Powder used in Polish Artillery in the 17th Century

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Abstract: Theoretical studies of the propulsion of a projectile in the barrel for a gun propellant system can be realized by numerically solving a system of equations that describe the phenomena occurring in the barrel space behind the projectile during firing. The accuracy of the solution of the mathematical model of the shot depends on reliable input data including the mass-geometric characteristics of the elements of the gun propellant system and the energy-ballistic characteristics of the gun propellant used. The present article addresses the problem of modelling the phenomenon of firing in a black-powder cannon from the 17th century. The acquisition of real input data, including the mass-geometric characteristics of the elements of the black-powder cannon is possible based on historical descriptions and preserved weapons in museums. In relation to the black powder used in 17th century artillery, although we have knowledge of the content of its components, there is no literature information on the value of its energy-ballistic characteristics. The purpose of this article is to determine the form of the burning rate law for the black powder used in Polish artillery in the 17th century and to compare the results obtained with available data on contemporary black powder. The procedure used was the so-called inverse solution of the gun interior ballistic model, in which, on the basis of the identified tactical-technical characteristics of the known black-powder cannon, the values of the force and covolume obtained by thermochemical calculations, and the assumed shape of the black powder grains, the values of the coefficient and exponent of the burning rate law were determined.

Keywords: internal ballistics, gun system, black powder, energy-ballistic characteristics

1 Introduction

The first attempt to describe the external effects of firings for gun systems was formulated by Benjamin Robins (1707-1751) in his work "New Principles of Gunnery" (1742). In the first chapter he presented a proposition to model the behaviour of smooth-bore, black powder guns firing lead or iron balls by formulating the following task: "*Given the dimensions of any piece of artillery, the density of its ball, and a quantity of its charge, to determine the velocity which the ball will acquire from the explosion, supposing the elasticity of the powder at the first instant of its firing to be given*" [1].

This was a period when black powder was the primary, and only, explosive, fulfilling the role of both initiating, propelling, and crushing material, and the construction of new weapon designs was based on experience resulting from the exploitation of weapons previously in use. The development of scientific thought, especially in the second half of the 19th century, and especially, among other things, the development of nitrocellulose and nitroglycerine gun propellants thanks to the invention of nitrocellulose (Schönbein, 1845) and nitroglycerine (Sobrero, 1847), the formulation of the balance of energy in the barrel during firing (Resal, 1864), and the equation of state of a real gas (Van der Waals, 1873), provided the theoretical basis for understanding and describing the phenomena occurring in the barrel during firing. For many years, the basic carrier of knowledge in the area of internal ballistics of gun propellant barrel systems were the monographs of Seriebriakov [2] and Corner [3].

Nowadays, theoretical studies of projectile propulsion in the barrel for a gun system are carried out by numerically solving a system of equations – formulated in both thermodynamic and gas-dynamic terms – describing the phenomena occurring in the barrel space (reaction chamber) during firing. The dependencies obtained for gas pressure and bullet velocity in the barrel on both time and bullet travel provide the basis for analysis and evaluation of: the strength and durability of barrels, recoil and jump of the weapon, loads on bolt assemblies and ammunition components, the operation of recoil brakes and recuperators and reloading mechanisms of automatic weapons. In addition, the determined projectile muzzle velocity is an input for modelling the motion of the projectile along its flight path.

The accuracy of the solution of the mathematical model of a shot - in the form of so-called ballistic curves – depends on reliable input data for the model. Considering the issue of modelling the phenomenon of a shot in a 17th century black-powder cannon, the problem concerns the acquisition of real input data, including the mass-geometric characteristics of the elements of the black-powder gun system and the energy-ballistic characteristics of the black powder. While the former are obtainable based on historical descriptions and preserved weapons in museums, obtaining reliable literature information on the energy-ballistic characteristics of black powder from the 17th century is not possible.

This is because the method of pyrostatic (closed vessel) testing of solid gun propellants used today [4], which allows the determination of data for modelling firing phenomena in the form of force, covolume and burning rate, was developed only in 1860 (Noble and Abel).

Taking the above into account, and due to the significant differences in the technology of black powder production today and in the 17th century, the authors of publications that have analysed experimental studies or modelling of the phenomenon of firing in a black-powder gun system have specific problems with the use of reliable data on black powder. For example, in publication [5], the subject of the analysis, of which was, among other things, strength calculations of the barrel (with an outlet diameter of 510 mm) of the Mons Meg bombard created in the 15th century, its authors unfortunately did not disclose the results of calculations in the field of internal ballistics and data on both the energy characteristics (force, covolume) and the form of the burning rate law of the black powder used. On the other hand, in publication [6], analysing the process of experimental testing of a 17th century musket with a caliber of 19.685 mm, its author used data on the properties of black powder obtained by modern research methods.

However, the mathematical model of the firing phenomenon – supported by the results of thermochemical calculations – provides an opportunity to apply the procedure of the so-called inverse solution of the gun interior ballistic model to a 17th century black powder cannon. On the basis of the known values of its geometric-mass characteristics and the projectile's range, the values of the energy characteristics of black powder obtained from thermochemical calculations, and the assumed values of the geometric-mass characteristics of the black powder grains, it is possible to determine the burning rate of black powder produced in the 17th century.

2 Research Object

In the 17th century, each country in Europe had its own separate system of gun classification. The first half of the 17th century in Poland was a period characterized by the ordering of artillery resources in technical and organizational terms. In 1637, the royal office of the Senior Gunner was created, which contributed to the revision of the number of cannons, their nomenclature and classification, and the standardization of the production process [7]. The classification of 17th century ordinary black powder cannons used in Poland is presented in Table 1. It was decided that the present object of research and analysis would be the double colubrine (Dragon). A replica of the colubrine is located in Golub Castle (Poland) [8]. To model the firing phenomenon, it is necessary to know the geometric and mass characteristics of this gun system. According to the Spanish artillery engineer Diego Ufano [7, 9] the double colubrine threw a 40-pound iron ball a distance of 8167 steps with a barrel elevation angle of 45^{o} (maximum range) and a distance of 682 steps with the barrel in the horizontal position. A step (or 2.5 foot) was equivalent to 0.72 m.

Table 1. Data for ordinary cannons (ordinary colubrines) used in Poland in the 17th century [7, 9]

Name (official and common) of the long-barrelled gun	Bullet weight [pound]	Cannon length (calibers)	Bullet's range [step]
Double colubrine (Dragon)	40	31	8167
Colubrine (Viper)	20	32	7140
Semi-colubrine (Snake)	10	33	5373
A quart of colubrine (Great Falcon)	5	34	4179
Octave of colubrine (Hawk)	2.5	35	3318

To load the barrel before firing, black powder of 4/5 of the bullet weight was used for coarse-grained powder or 2/3 of the bullet weight for very fine-grained powder. The barrel length of this cannon is 31 calibers (equivalent to 20 feet), and by caliber was meant the diameter of the barrel's muzzle.

Table 2 presents the SI values of the geometric-mass characteristics of the double colubrine and the maximum range of the cannonball, based on the Hartmann cannon gauge, developed in 1540 and quickly popularized in Europe [7], in which the Nuremberg pound (with a mass of 509.96 g) was used to calculate the weight of the cannonball, and also assuming the Old Polish system of measurements, in which a foot is 0.288 m, and the fact that in the Polish artillery of the time, cannonballs were made of iron (as opposed to the cast iron balls used in the Swedish artillery).

Table 2. Geometric-mass characteristics and maximum range of the double colubrine

Parameter	Value
Barrel length [m]	5.76
Barrel diameter (caliber) [m]	0.186
Ball mass [kg]	20.4
Diameter of the ball [m]	0.172 [10]
Black powder weight [kg]	16.3
Maximum range [m]	5880

The powder chambers of cannons were usually constructed in three different shapes (Figure 1), for which the determinant was the caliber of the bullet (ball) [9]. The most common shape of the powder chamber was an equal chamber with a diameter equal to one caliber and a length equal to four calibers. This shape of powder chamber was adopted here for further consideration.

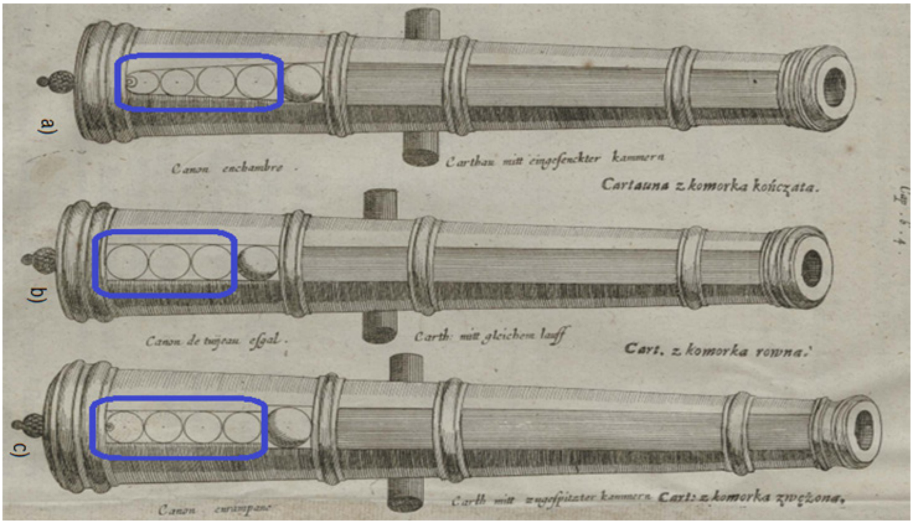

Figure 1. Shapes of powder chambers (marked in blue) of 17th century cannons: terminating chamber (a), equal chamber (b) and tapered chamber (c) [9]

3 Research Material

Black powder is the oldest propelling explosive. It is a mechanical mixture of potassium nitrate(V) (KNO_3), charcoal, and sulfur. Today, the percentages of these components are approximately 75%, 15% and 10% by mass, respectively. However, the percentage composition of potassium nitrate, charcoal and sulfur in black powder has changed over the centuries (Table 3).

Table 3. Composition of black powder over the centuries (in %)

A component of black powder	13th century (Bacon) [11]	17th century (Siemienowicz) [12]		19th century (Berthelot) [13]
		Artillery	Small arms	
KNO_3	37.5	66.6	78.7	74.64
Charcoal (C)	31.25	16.7	9.5	13.51
Sulfur (S)	31.25	16.7	11.8	11.85

Detailed information on the composition and properties of black powder between 1340 and 1450 is presented in [14]. At that time, in the recipes for the production of black powder, one can find various mass ratios: KNO_3 to sulfur (from 2:1 to 16:1), as well as KNO_3 to charcoal (from 1:1 to 8:1). The authors of the above publication made samples of black powder based on the collected recipes (but using contemporarily produced ingredients) and determined the heat of combustion, and conducted differential scanning calorimetry (DSC) studies. Their subject of analysis, however, was not the energy-ballistic properties directly useful for modelling the firing phenomenon.

The first mention of black powder production in the Polish lands dates back to the 14th century [15, 16]. According to documented literature and unconfirmed oral accounts, black powder was produced in Legnica and in the vicinity of Ogrodzieniec (near Częstochowa). The technology for making black powder in the 15th-17th centuries consisted of two basic steps [17]:

1) Grinding the ingredients of black powder with a small amount of water.
2) Mashing the thick paste through a sieve and then drying the resulting grains.

Initially, these operations were performed by hand (Figure 2), but with the advancement of technology, grinding of black powder components was carried out in stamp mills. The grinding elements of a stamp mill were palfreys lifted up by arms attached to a rotating wooden shaft. The shaft was either driven by hand or by a water wheel. The palfrey, falling into a cylindrical chamber, mixed, crushed and whisked the powder components inside (Figure 3).

The palfrey, falling about 30 times per minute, mixed and whisked the black powder mixture for 10 to 12 h. The resulting compacted wet mixture was mashed through a brass sieve, and the resulting black powder grains were dried in the sun to a water content of less than 1%. The dried black powder grains were sieved on screens, dividing them into the desired grain fractions.

Figure 2. The process of grinding the black powder components in a mortar (on the left) and mashing the paste through a sieve (on the right) [16, 17]

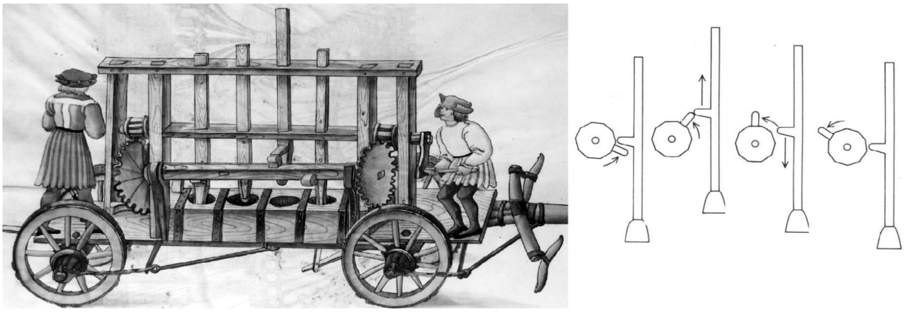

Figure 3. Transportable gun powder stamp mill and diagram of its operation [16]

At that time, evaluation of the functional characteristics of black powder was carried out by indirect methods, without formulating any mathematical relationships. Examples of such an evaluation were measurements of the:

– amount of deformation of the lid of a closed vessel in which the black powder was burned (Bourne, 16th century),
– range of bullets fired from a given type of weapon, in which similar weights of different black powders were used (Luys Collado, William Eldred, Nathanian Nye, 17th century), or
– measurement of the height of the toss of a certain mass under the effect of burning the black powder under test in a vertically placed mortar [7].

We are not able therefore to extract from the available literature data on the energy-ballistic characteristics (force, covolume, burning rate law) of black powder manufactured in the 17th century, but we can say with full confidence that they differed from black powder produced today, as influenced by the following factors:

– different (compared to modern) percentage composition of black powder components (Table 3),
– methods used in the 17th century for obtaining and purifying KNO_3 [16, 17],
– the type of wood used during charcoal burning [18],
– giving the black powder mass the right density in the manufacturing process.

Soft wood was best suited to produce black powder. It was obtained from deciduous trees. However, the type of wood used to produce charcoal also affects the burning rate (Figure 4).

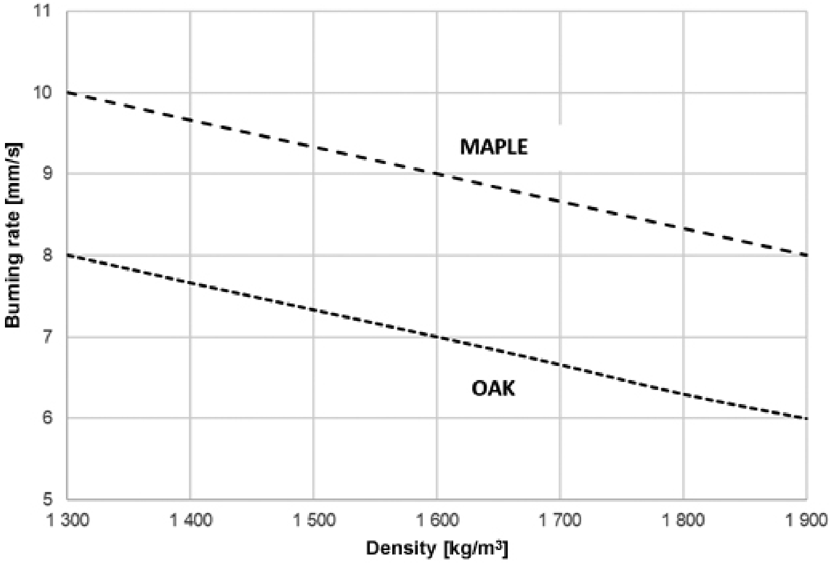

Figure 4. Influence of wood type on the burning rate of black powder (based on [18])

The process of pressing black powder pulp in squashes with a significant impact on the increase in black powder density did not occur until the second half of the 18th century [6, 19]. Table 4 gives the approximate pressure values needed to obtain black powder with the appropriate density [11, 16, 19].

Table 4. Dependence of black powder density on pressing pressure

Pressure [MPa]	2	3.3	6.6	13.3	20	33.3	50
Density [kg/m^3]	1320	1410	1550	1695	1775	1840	1880

Direct confirmation of the effect of black powder density on its burning rate is provided by the results of research published in [19]. Figure 5 presents two graphs of burning rate as a function of gas pressure. Graph A shows the change in burning rate of black powder pressed at 20 MPa in the manufacturing process, while graph B shows the burning rate of black powder pressed at a pressure of over 400 MPa.

The available literature shows that the size and geometric shape of black powder grains used depended on the type of weapon. Black powder used in small arms [6] was marked by an irregular geometric shape of the grains and was classified as fine-grained powder (about 1-2 mm in diameter) and coarse-grained powder (about 2-6 mm in diameter). By contrast, the grains of black powder used in artillery resembled the shape of a cuboid with side dimensions in the range of 8-16 mm [20].

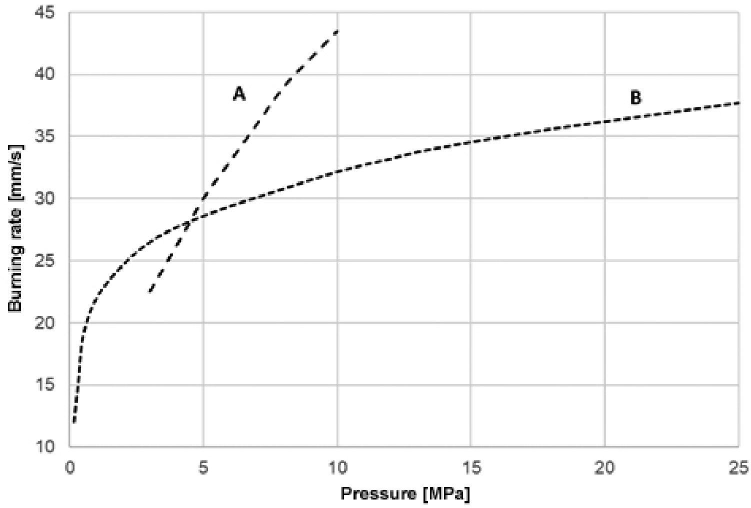

Figure 5. Burning rate of black powder as a function of gas pressure (based on [19])

It was not until the second half of the 19th century that Van der Waals formulated the equation of state of a real gas, and Andrew Noble and Frederick Abel developed an experimental method for testing black powder in a closed vessel (manometric), along with recording the pressure of the gases formed after burning a given mass of powder, which made it possible to determine the energy-ballistic characteristics of gun propellants in the form of force, covolume and burning rate, used today for analysis and modelling of internal ballistics phenomena.

4 Test Method

The authors of this publication set out to determine the form of the burning rate law of black powder used in Polish artillery in the 17th century and to compare numerically the results obtained with available data on contemporary black powder. The procedure of the so-called inverse solution of the gun interior ballistic model was used, which is based on:

- the values of geometric and mass characteristics of the black powder system (double colubrine) and data on the projectile's range (according to Table 2),
- the values of the force and covolume of black powder used, according to Siemienowicz's description (Table 3) in the Polish artillery in the 17th century, resulting from thermochemical calculations,
- the assumed density of black powder and the assumed shape of its grains.

The values of the coefficient and exponent of the burning rate law will be thus determined.

5 Test Results

5.1 Thermochemical calculations

The CHEETAH thermochemical code [21] with the BLAKE database [22] was used to determine the ballistic parameters of black powder. The BLAKE database was extended with three solid components: K_2S, K_2SO_4 and K_2CO_3. Thermochemical data for these constants were taken from [23]. Black powder was assumed to have the following mass composition: 66.6% KNO_3, 16.7% charcoal and 16.7% sulfur. Data for the components of black powder necessary for the thermochemical calculations are collected in Table 5 [23, 24].

Table 5. Data for thermochemical calculations [23, 24]

Component (Chemical formula)	Density [g/cm^3]	Molar mass [g/mol]	Molar volume [cm^3/mol]	Enthalpy of formation [cal/mol]
KNO_3	2.11	101.10	47.915	–118070
Charcoal ($C_{10}H_{4.774}N_{0.039}O_{1.234}$)	0.5	145.429	290.858	–8604
Sulfur (S_8)	1.96	256.48	130.857	0

During experimental testing of a 17th century musket [6] using black powder of different grain sizes, the maximum gas pressures obtained in the space behind the projectile were in the range of 20-40 MPa, and these pressures guaranteed the expected projectile muzzle velocity of the bullets. The strength calculations performed for the barrel of the Mons Meg bombard [5] showed that the maximum pressure of black powder gases not causing damage to the barrel could not exceed 87 MPa. Taking the above data into account, thermochemical calculations were carried out for black powder of a given composition for simulated pyrostatic test conditions, for which a loading density of 200 kg/m^3 was assumed to guarantee a maximum pressure of several tens of MPa. The results obtained: the maximum pressure p_{max}, the isochoric combustion temperature T_v of the black powder gases and the number of moles n_g of gaseous products formed, made it possible to determine the values of the energy characteristics of the black powder – necessary for modelling the phenomenon of firing from a black-powder system – using the following relations [25]:

– for the force (f):

$$f = n_g R T_v \quad (1)$$

where R is the universal gas constant,

– for the covolume of gaseous combustion products (η):

$$p_{max} (v - \eta) = n_g R T_v \quad (2)$$

In addition, the thermochemical calculations also make it possible to determine other thermochemical parameters such as:

– the ratio of the specific heat of a gaseous mixture at constant pressure to the specific heat at constant volume under conditions of "freezing" of the composition of the products of combustion at the temperature of combustion:

$$\kappa = \frac{C_p}{C_v} \quad (3)$$

– the internal (ballistic) energy of the combustion products treated as a perfect gas:

$$E_b = \frac{f}{\kappa - 1} \quad (4)$$

– the molar mass of the black powder gases M_s.

The results of the thermochemical calculations performed are summarized in Table 6.

Table 6. Thermochemical calculation results for a loading density of 200 kg/m^3

Parameter	Value
Pressure p_{max} [MPa]	69.9
Isochoric combustion temperature T_v [K]	2047
Number of moles n_g [mol/kg]	17.61
Force f [J/g]	299.6
Covolume η [cm^3/g]	0.539
Specific heats ratio c_p/c_v	1.121
Ballistic energy E_b [J/g]	2400
Molar mass of black powder gases M_s [g/mol]	56.796

5.2 Ballistic calculations

The thermodynamic interior ballistic model with global parameters [26, 27] was used in ballistic calculations in which the procedure of the so-called inverse solution of the mentioned gun interior ballistic model was used to determine the value of the coefficient β and exponent α of the power form of the burning rate law.

$$r = \beta \cdot p^{\alpha} \quad (5)$$

The following input data were used in the calculations:

– the values of the geometric and mass characteristics of the black powder system (double colubrine) and the data on the projectile's ranges (Table 2),
– the muzzle velocity v_m = 605 m/s of a 20.4 kg cannonball guaranteeing maximum range, calculated from the solution of the external ballistics model for normal atmospheric conditions,
– the thermochemical calculation results for black powder with a mass composition of KNO_3 66.6%, charcoal 16.7%, and sulfur 16.7% (Table 6),
– the shape of the black powder grain: a cube with sides (web sizes) equal to 8, 9 and 10 mm (the thickness of the combustible layer e_1 equal to 4.0, 4.5 and 5.0 mm, respectively),
– the density of black powder not greater than 1600 kg/m^3.

The two-parameter equation of the burning rate law (Equation 5) requires – when modelling the firing phenomenon - taking a certain value of one of the parameters. It was decided that this parameter would be the exponent α. An analysis of available specialized literature on the specifics of black powder combustion, *e.g.* [2, 5, 18, 19, 28-31], showed that this exponent can vary in the range of 0.133-0.671. However, it is not possible to unambiguously determine the conditions of applicability of a specific value of this exponent because the research was on black powder from different manufacturers, with different grain sizes and densities, and the research itself, being experimental (in a closed vessel), was performed for different loading densities, which was reflected in the gas pressure ranges taken for analysis, such as 0.5-2.7, 2.5-25 or 0.5-300 MPa.

Taking the above into account, it was decided to calculate the value of the β coefficient for the exponent α in the range of values 0.2-0.6. Figure 6 presents ballistic curves in the form of graphs of gas pressure $p(t)$ in the space behind the projectile and a cannonball velocity $v(t)$ in the barrel for a specific variant of the data characterized by the thickness of the combustible layer e_1 = 4.5 mm and exponent α = 0.4.

For the variants of the web size $2e_1$ in the range of 8-10 mm and the exponentα in the range of 0.2-0.6, as well as the assumed muzzle velocity of the cannonball of 605 m/s with a deviation of ±0.1%, the range of changes of the maximum pressure p_{max} of gases in the space behind the projectile resulting from the simulation of the firing was in the range of 56.8-58.6 MPa. This is a typical pressure for black-powder gun systems as confirmed by available literature data. For the assumed web size $2e_1$ and the exponent α, the plots of the coefficient β are presented in Figure 7 and listed in Table 7.

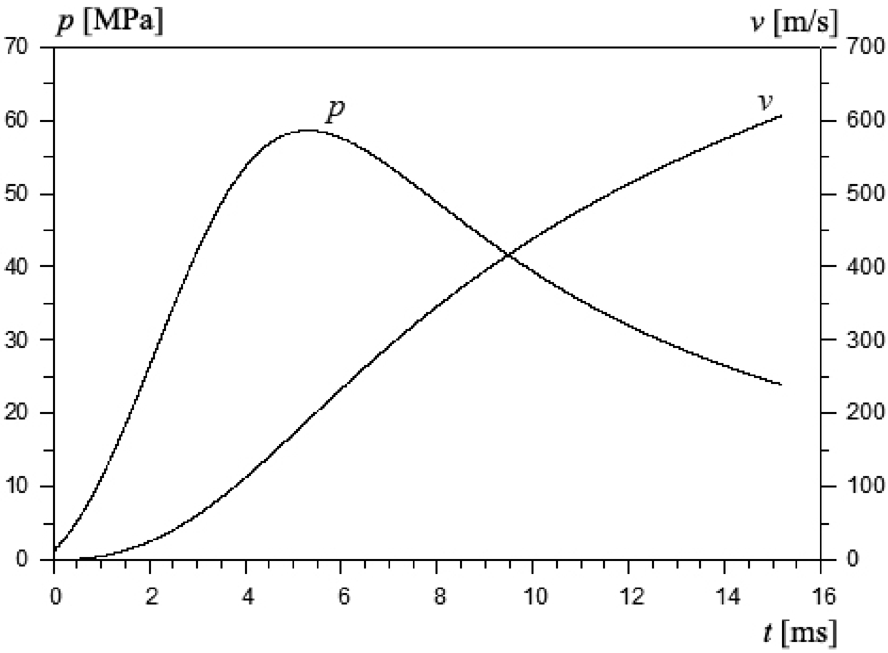

Figure 6. Ballistic curves $p(t)$ and $v(t)$ for the thickness of the combustible layer e_1 = 4.5 mm and exponentα = 0.4

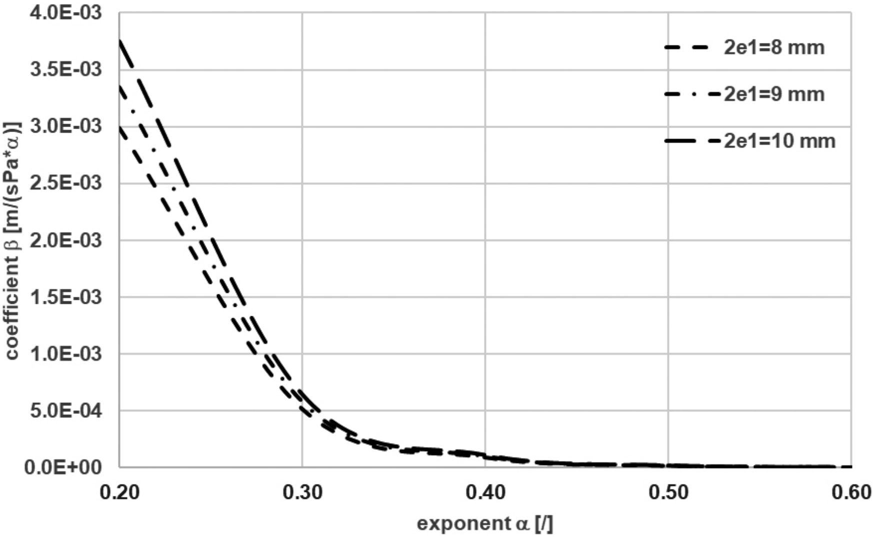

Figure 7. Plots of $\beta = f(\alpha)$ for various web sizes $2e_1$

Table 7. Values of β [m/(s·Pa$^{\alpha}$)]

Web size $2e_1$ [mm]	Exponent α				
	0.2	0.3	0.4	0.5	0.6
8	0.00299	0.000515	0.0000890	0.0000153	0.00000266
9	0.00335	0.000580	0.0000995	0.0000172	0.00000299
10	0.00375	0.000644	0.0001110	0.0000192	0.00000332

The resulting values of the coefficient β and the assumed values of the exponent α were the basis for determining, according to Equation 5, the burning rate graphs $r(p)$. Figures 8 and 9 present the burning rate plots determined for two extreme values of the exponentα (0.2 and 0.6) and for different values of the web size $2e_1$.

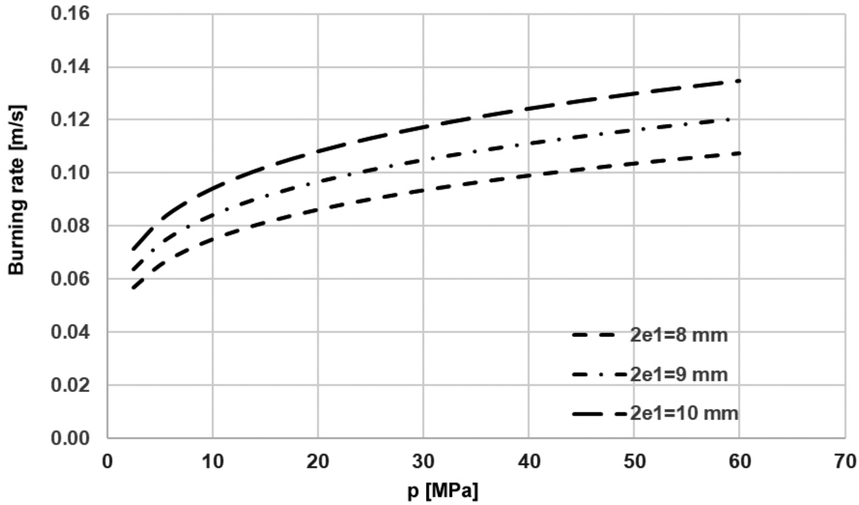

Figure 8. Plots of *r(p)* for the exponent $\alpha = 0.2$ for different web size $2e_1$

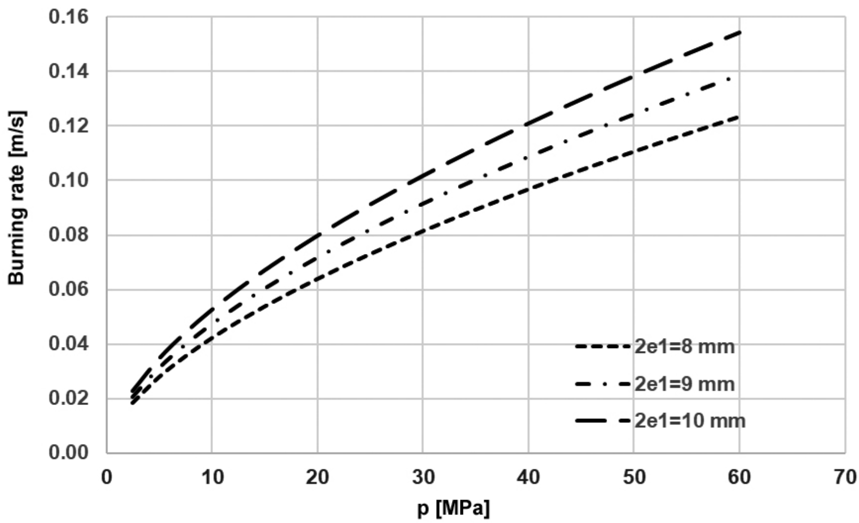

Figure 9. Plots of *r*(*p*) for exponent$\alpha = 0.6$ for different web size $2e_1$

6 Results and Conclusions

To determine the value of the coefficient β in the power form of the burning rate law (Equation 5) for the black powder used in the Polish artillery in the 17th century, the procedure of the so-called inverse solution of the gun interior ballistic model was used, with the following known input data:

- the values of geometric and mass characteristics of the gun system (double colubrine) and the data on the projectile's range (according to Table 2),
- the values of the force and covolume of the black powder used according to Siemienowicz's description (Table 3) in the Polish artillery in the 17th, resulting of thermochemical calculations, and
- assumptions about: the black powder density, grain shape and dimensions, and the range of the exponent α.

This study shows that it is possible to perform simulation analysis of firing in a black-powder gun for a wide range of values of the exponent α and the corresponding value of the coefficient β. The burning rate plots obtained are compared in Figure 10 with literature data [19], where the results of a study of the burning rate of samples of black powder pressed at a pressures of 20 MPa (Price, Juhasz) and 400 MPa (Bielaev) are presented. The $r(p)$ plots, – both for $\alpha = 0.2$ and for $\alpha = 0.6$, are above the area of $r(p)$ values for black powder pressed at 20 MPa, which would suggest a lower pressing pressure for the powder analysed.

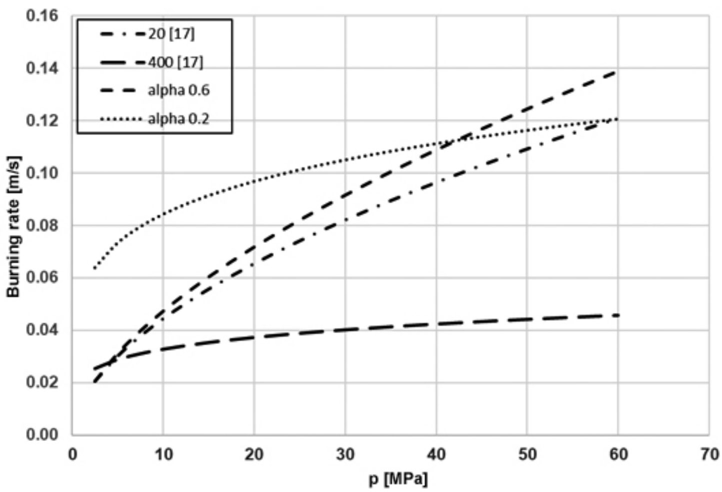

Figure 10. Comparison of $r(p)$ plots of black powder obtained by simulation (denoted as alpha 0.2 and alpha 0.6 for which $2e_1 = 9$ mm), and those obtained from literature data [19] for different pressing pressures

Figure 10 was further supplemented with the results of experimental studies [19] on the burning rate of black powder with densities in the range of 1430-1900 kg/m^3 (Figure 11). Experimental studies were conducted in the pressure range of 0.45-13.5 MPa (White, Sasse), hence in Figure 11 the range of burning rate was limited to 0.1 m/s and the range of pressure was limited to 16 MPa. An analysis of both figures shows that it makes more physical sense to have a condition in which the value of the exponent α is equal to 0.6 rather than 0.2. This is consistent with the information in [32], in which it was determined that the exponent α for black powder with a density of 1900 kg/m^3 reaches values in the range of 0.25-0.35. The value of this exponent increases as the density value decreases, and for example, for a density of 1700 kg/m^3 the exponent α reaches values in the range of 0.45-0.55.

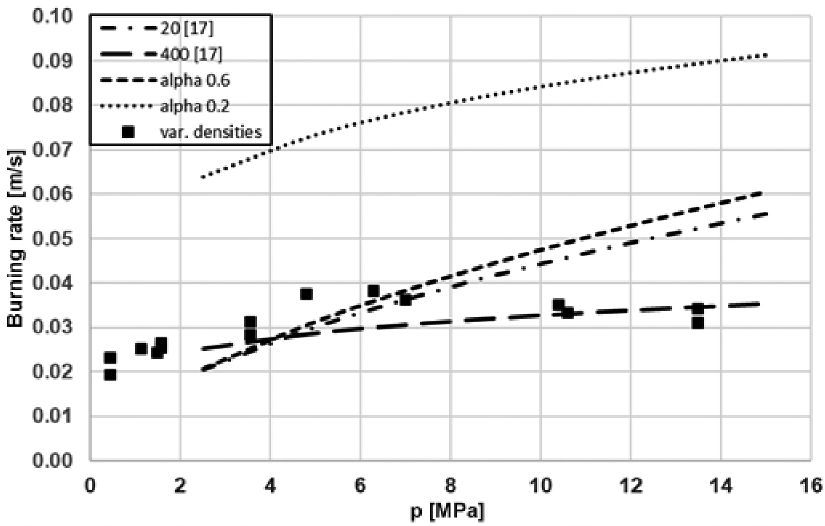

Figure 11. Comparison of $r(p)$ plots of black powder obtained by simulation (denoted as alpha 0.2 and alpha 0.6) and those obtained from literature data [19] for different densities of black powder

In addition, a comparison was made between the burning rate of nitrocellulose porous combustible material (nitrocellulose 47.5%, cellulose 27.5%, binder 12.5%, stabilizer 1%, and other 11.5%.) with a density of about 800 kg/m^3, used for artillery ammunition shells, and the burning rate of the analysed black powder. As a result of closed vessel tests [33], values of the coefficient $\beta = 8.92 \cdot 10^{-5}$ m/(s·MPa$^{\alpha}$) and the exponent $\alpha = 1.9$ were determined for the power-law form of the burning rate. The results of the comparison are presented in Figure 12.

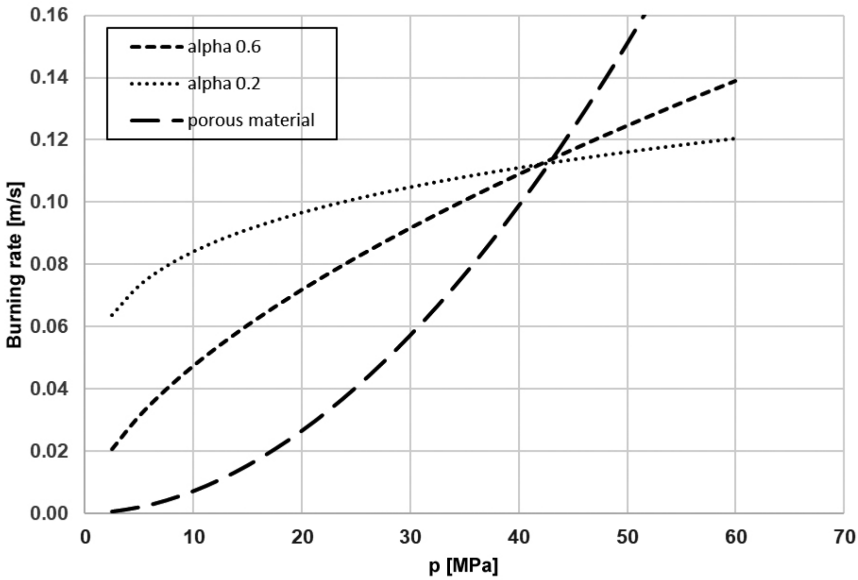

Figure 12. Comparison of $r(p)$ plots of black powder obtained by simulation (denoted as alpha 0.2 and alpha 0.6) and nitrocellulose porous combustible material

Nitrocellulose-based porous material in the region of low pressures (below 40 MPa) has a significantly lower burning rate than black powder, which confirms the validity of using black powder as an ignition material in general.

The authors of this article are aware that the most objective method for determining the actual value of the coefficient β and the exponent α of the power form of the burning rate law of black powder used in the 17th century is to carry out closed vessel tests with black powder made from the ingredients available at that time and according to the procedure of that time.

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Contribution

Leciejewski Z.: conception, performing the statistical analysis
Surma Z.: methods, performing the numerical calculations
Trzciński W.: methods, performing the therochemical analyses
Biegańska J.: other contributions to the publication
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