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The influence of gunpowder manufacture method on its detonative force

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Abstract

Gunpowder was manufactured by (the wet process) of dissolving potassium nitrate (KNO_3) in hot water, followed by the addition and wetting of charcoal and sulfur, while the KNO_3 was in its dissolved state. The water was then evaporated, and the granular solid mass was dried, then ground. This was followed by the downstream process. Alternatively, gunpowder was manufactured by (the dry process) of mixing and grinding the dry ingredients together, followed by the downstream process. The downstream process involved the wetting of the mass with water; which either did - or did not - incorporate dextrin as a binder; and passed through either a #12 or a #16 sieve before being allowed to dry. These two processes, with the three factors of dissolved KNO_3, binder or sieve size were incorporated into a 2^3 DOE matrix, with the responding or dependent variable being the velocity of a cannonball shot using a particular DOE batch of gunpowder. A novel method of recording sound, using the Audacity® software was utilized for calculating the deflagration time, speed and the frequency-amplitude profile of the cannonball for each batch. The presence of binder and the homogeneity of mixing of the ingredients on a molecular scale (wet process) exerted the most influence on the velocity of the cannonball; although neither was statistically significant. The greatest speeds were obtained using the gunpowder manufactured by the wet process, in the presence of the binder. The cannonball speed was inversely correlated with the deflagration time of the gunpowder. Normalized amplitude graphs for gunpowder batches within a selected frequency range were reminiscent of overpressure - blast model plots, indicating that high resolution sound input could serve as a surrogate for pressure transducer monitored blast regime interpretation. An amplitude-frequency parameter was derived which could predict the cannonball velocity for any batch with reasonable accuracy. In our experimental regime, the detonative power of the gunpowder was independent of granule size; at least within a range of 0.85 mm to 1.7 mm. It was dependent on the intimacy of molecular mixing of the three ingredients as well as on the presence of binder. The deflagration time of the gunpowder as well as its amplitude-frequency derived parameter showed similar dependencies on the independent variables.

Keywords

Gunpowder, Black powder, Detonative force, Manufacture, Audacity, Sieve, Molecular mixing, Binder, Deflagration time, Cannon

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Introduction

Although gunpowder has been superceded by high explosives, it still enjoys a niche use in fireworks, science demonstrations and amongst enthusiasts. There is always a chance of mechanisms remaining undiscovered, when a nascent technology becomes obsolete, while still in its heuristic stage. Black powder eminently lends itself to this misfortune, as evidenced by manuscripts that endeavor to unravel its efficiency, detonative force and/or explosive mechanisms; dating back almost a century (1, 2). Since mechanisms are almost invariably immune to anachronism, and agnostic of specific methodology, an investigation into the mechanisms by which gunpowder deflagrates or detonates is likely to prove useful in the field of explosives in general; without incurring anachronistic disadvantage.

A systematic study of black powder with regard to the various factors that can influence its explosive power is still lacking. Conventional wisdom passed down from (interpretations of) medieval texts and the experience of enthusiasts in internet forums is generally regarded as true and serves as a self-fullfilling empirical prophetic, instead of a mechanism-centric thorough approach. The objective of this work is to plug this gap to increase the basic understanding of the science of explosives in general, and that of gunpowder in particular.

Materials

The cannon was fabricated from a 1 inch Poly Vinyl Chloride (PVC) pipe cut to a length of 9.5 inches. A size 6 solid rubber stopper was glued to one end of the pipe such that the bottom of the stopper was flush with the PVC pipe with 1 inch of the stopper glued inside the PVC surface with JB WELD™ epoxy glue, manufactured by J-B Weld company, Sulfur springs, TX, USA. A hole was drilled 1.5 inches from the end of the stoppered PVC pipe end with a 1/16 th inch drill bit to accommodate the fuse. The cannonball was a 1 inch chrome stainless steel ball, weighing 65 g, purchased from Amazon.com. The 2 mm diameter fuse was also purchased from Amazon.com. A Labconco chemical fume hood, Labconco corporation, Kansas City, MO, USA, was used to dry the gunpowder.

The KNO_3, part no. P0074, lot no. 506246, and Sulfur, part no. S0138, lot no. 217689, were purchased from Flinn Scientific, Batavia, IL. The Charcoal, part no. CH8068 was purchased from Skylighter Inc., Purcellville, VA. The 8 inch diameter sieves (# 12, # 16 and #20) were purchased from Amazon.com, manufactured by KimLab made of 304 Stainless Steel Wire Cloth, Chorme Plating Frame. The Great Value Ziploc® sandwich bags were purchased from a local Walmart store.

The Design Of Experiments (DOE) was run on Minitab version 19.1.1 (64-bit) manufactured by Minitab LLC, State College, PA, USA. Sound was recorded on Audacity®, version 3.1.3, an open-source, free cross-platform software for recording and editing sounds, executed on a Lenovo Ideapad® 3 with Intel® Core™ i3-1115G4 @ 3.00GHz × 4, running Ubuntu 20.04.6 LTS.

Methods

A full factorial experiment was designed according to Table 1. The experiment consisted of three potential factors; that could affect the response variable. Those factors were; whether the KNO_3 was dissolved in water when the other ingredients were added, whether the gunpowder formulation contained binder and whether the gunpowder was passed through sieve size # 12 or seive size # 16. The response variable was the speed of the cannonball achieved with that batch of gunpowder. The factorial experiment design is presented in Table 1. The same lot of chemicals were used throughout the study. At least two replicates of each batch of gunpowder were tested.

Table 1: Factorial design of experiments, 2 levels and 3 factors: 2^3=8 experiments

Experiment number	KNO_3	Sieve size	Binder
1	+	+	-
2	+	+	+
3	+	-	-
4	+	-	+
5	-	+	+
6	-	-	+
7	-	-	-
8	-	+	-

KNO_3: Positive =mixed with other ingredients while in its dissolved aqueous state, Negative =mixed with other ingredients in its solid state
Sieve size: Positive = passed through 1.7 mm opening, sieve size # 12, Negative = passed through 0.85 mm opening, sieve size # 16
Binder: Positive 1.2% to 2.6% w/w dextrin, Negative = 0% w/w dextrin

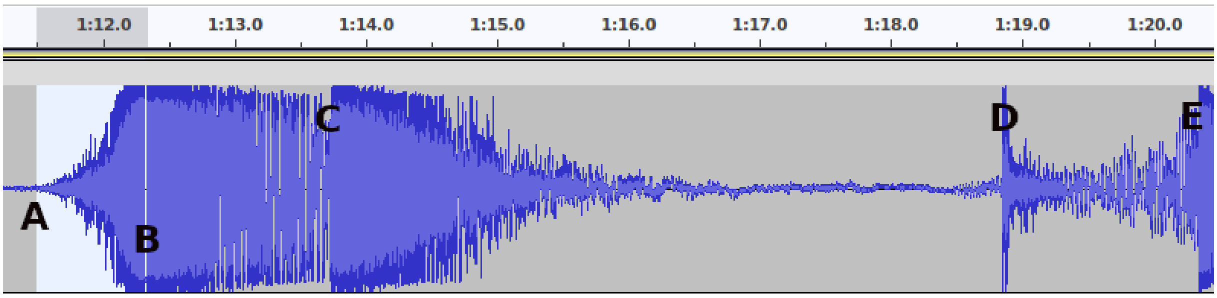

Figure 1a: A representative sound profile (speed of profile is decreased 10X) of the cannonball's time to hit the target as recorded with the application Audacity®. The depicted sound profile is from file E4T1.aup (see supplementary files). The point A represents the 'hissing' sound of the gunpowder as it burns. The point B represents the sound when the gunpowder explodes. The time from point A to point B is the deflagration time (white block in figure and column 4 in Table 2). The point C represents the sound when the cannonball hits the target whiteboard. The time from point B to point C is the time taken for the cannonball to hit the target (column 2 in Table 2). The points D and E represent the sound when the cannonball ricochets off the target whiteboard and falls to the floor.

Figure 1b: The deflagration time of the gunpowder as reported by Audacity® (File E4T1.aup). The time between the start of the 'hissing sound' and the time the gunpowder explodes (between points A and B in Figure 1a). The time is 0.732 seconds. Since; for ease of display and calculation purposes, the speed is slowed by a factor of 10, the actual deflagration time for the gunpowder prepared for experiment 4, trial 1, was 0.0732 seconds (see Table 2, average deflagration time for experiment 4).

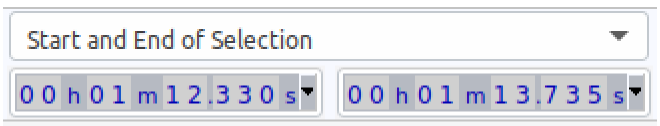

Figure 1c: The time for the cannonball to hit the whiteboard as reported by Audacity® (File E4T1.aup). The time between when the gunpowder detonates and the time the cannonball hits the whiteboard (between points B and C in figure 1a). The time is 1.405 seconds. Since; for ease of display and calculation purposes, the speed is slowed by a factor of 10, the actual time for the cannonball propelled by the gunpowder prepared for experiment 4, trial 1, was 0.1405 seconds (see Table 2, average time for experiment 4).

We did not have access to a high speed camera or other automatic device to measure the speed of the cannonball. Hence we used the application Audacity®, an open-source, free cross-platform software for recording and editing sounds. Version 3.1.3, was capable of a precision of 1 millisecond, or 0.001 seconds. The sound profiles of all the gunpowder batches (1 through 8) run at at 0.1X speed were analyzed by clicking the 'analyze' tab, then clicking on 'Plot Spectrum' from the dropdown menu. A representative spectrum (analyzed from the data in E4T1.aup) is shown in Figure 2 below.

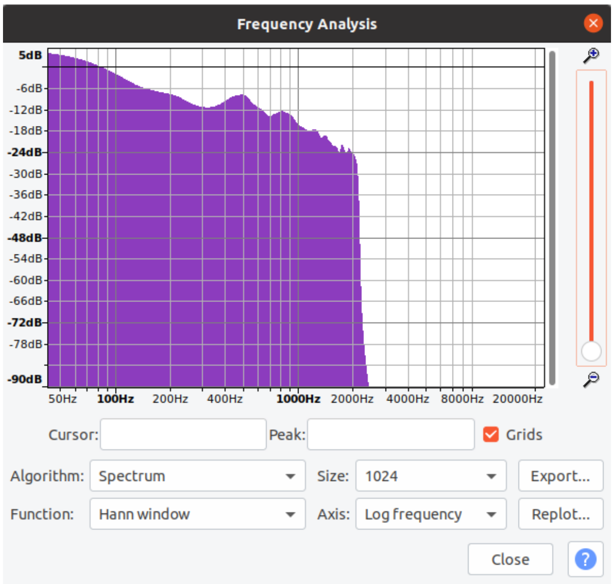

Figure 2: A representative spectrum from the analysis of the data in E4T1.aup. The spectrum plots the decibel sound levels across a range of frequencies.

The spectra of all the gunpowder batches were exported as text files using the 'export' button and imported into Libreoffice Calc, Version: 6.4.7.2 Build:1:6.4.7-0ubuntu0.20.04.7,
The Document foundation, Debian and Ubuntu. The data points extended across frequencies ranging from 43.066 Hz to 21.96 KHz. Figure 3 shows the frequency-amplitude graph plotted across these frequency ranges for the eight gunpowder batches.

Gunpowder fraction < Sieve #16

After the gunpowder was used for the cannon experiments, the remaining amount was weighed and passed through a #16 sieve. The gunpowder was poured on an inverted #16 sieve, placed on a paper towel. The sieve was moved to-and-fro 10 times between two marks on the paper towel spaced two inches greater than the edge of the sieve on either side. The amount of the gunpowder that passed through the #16 sieve and collected on the paper towel was weighed. Finally, the percent fraction of the prepared gunpowder that passed through the # 16 sieve was calculated.

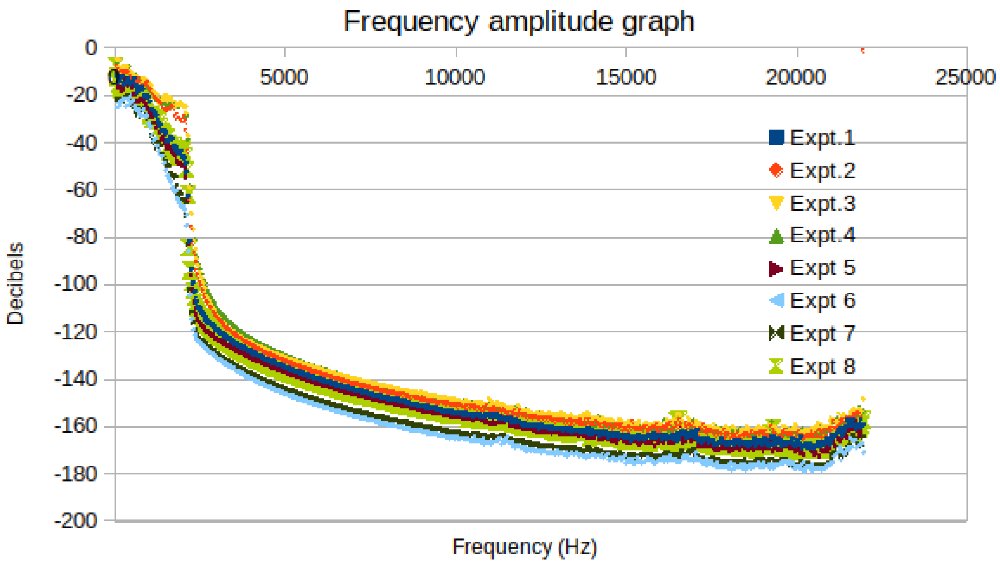

Figure 3: A frequency amplitude plot for the range of frequencies analyzed by the Audacity® software.

Experiments with undissolved KNO_3

For experiments numbered 5 through 8, where KNO_3 was in its undissolved state when mixed with the other ingredients, the process of gunpowder preparation started by crushing the KNO_3 using a mortar and pestle until the powder so obtained was sufficiently small to pass through a #20 sieve. 30 g of this sieved KNO_3 powder was combined with 6 g of charcoal and 3 g of sulfur in the Ziploc sandwich bag. The bag was inverted 150 times to mix the contents together. The bag was opened and the contents emptied into a 5.5 inch X 5.5 inch square polystyrene weighing dish. Sufficient distilled water was added using a wash bottle with simultaneous kneading until the contents reached a dough-like consistency; i.e. the mass could be fashioned into a single ball without falling apart. When the experiment called for a binder to be added, the distilled water was substituted with a 10% w/w dextrin solution in water. The amount of water or 10% w/w dextrin solution added was calculated by subtracting the final weight of the appropriate solution in a wash bottle from its initial weight.The 'dough' was then passed through the sieve size assigned in the DOE for that experiment and collected on a paper towel kept underneath. The wet granules were placed in the chemical fume hood, with the opening set to 4 inches and the blower on, to dry for 12 to 20 hours.

Experiments with dissolved KNO_3

For experiments numbered 1 through 4, where KNO_3 was in its dissolved state when mixed with other ingredients, the process of gunpowder preparation started by dissolving 30 g of KNO_3 at a temperature below boiling in 30 mL of distilled water in a 1 L beaker. Once dissolved, 6 g of charcoal and 3 g of sulfur were added and wetted in the KNO_3 solution. The suspension was heated until a granular dough-like consistency was obtained, at which point, it was transferred to the chemical fume hood. The dough-like mass was allowed to dry overnight without the vent fan on. It was then crushed using a mortar and pestle to a powder-like consistency that was free from large particles. It was then transferred to the polystyrene weighing dish. The dough was then wetted with either water (experiments 1 and 3), or with 10% w/w dextrin solution (experiments 2 and 4) and mixed until it could be fashioned into a single solid mass. It was then passed through the sieve size assigned in the DOE for that experiment and collected on a paper towel placed underneath. The wet granules were placed in the chemical fume hood, with the opening set to 4 inches and the blower on, to dry for 12 to 20 hours.

Firing the cannon

Before every test run, the cannonball was loaded, and ejected out of the cannon several times by manually tilting the cannon to ensure that there were no obstructions to the movement of the cannonball while inside the cannon. There was no significant friction between the cannonball and the inner diameter of the PVC pipe. The cannon was filled with 5 g of black powder, then the fuse was inserted through the hole into the black powder. The cannonball was rinsed with water and dried thoroughly before loading. The cannon was sloped gently to allow for the cannonball to roll slowly into the cannon onto the black powder. The front end of the cannon was firmly grasped and held on a table so that the elevation of fire was equal to the angle made by the back end of the cannon resting on the table and the front end of the cannon resting on the encircled fingers around it (approximately 10^{o}). The distance from the front end of the cannon to the target was 2.75 meters.

Statistical significance

Results were considered statistically significant at $p < 0.05$.

Results

Table 2: Various measured attributes of the gunpowder batches

Experiment number	Average Time (seconds) ± SD	Speed of cannon ball (m/sec)	Deflagration time (seconds) ± SD	Amount of water or 10% w/w dextrin solution added[1] (g)	Percent passed through sieve fraction #16
1	0.348 ± 0.035	7.9	0.1132 ± 0.0064	6.2	20.8
2	0.132 ± 0.011	20.7	0.0862 ± 0.0067	4.8	26.1
3	0.323 ± 0.00	8.5	0.0929 ± 0.0007	7.1	25.8
4	0.127 ± 0.021	21.5	0.0789 ± 0.0057	6.2	38.5
5	0.306 ± 0.027	8.9	0.1123 ± 0.0177	6.8	10.9
6	0.325 ± 0.00	8.4	0.1200 ± 0.0132	10.0	40.0
7	Not measurable[2]	0.6[3]	0.1600 ± 0.0146	7.7	64.2
8	0.450 ± 0.015	6.1	0.1303 ± 0.0130	9.0	22.9

1. to wet the mass to a dough.
2. Cannonball did not travel the distance to the whiteboard, instead ejecting out of the cannon and falling to the floor.
3. The speed was assumed to be an order of magnitude lesser than experiment 8 since the explosive power of the gunpowder batch was not enough to propel the cannonball the distance between the cannon and the whiteboard (see 2 above). The cannonball instead hit the drywall below the whiteboard. This value was input into the DOE.

Coded Coefficients

Term	Effect	Coef	SE Coef	T-Value	P-Value	VIF
Constant		10.290	0.785	13.11	0.048	
nitrate	8.270	4.135	0.785	5.27	0.119	1.00
sieve size	1.920	0.960	0.785	1.22	0.436	1.00
binder	8.920	4.460	0.785	5.68	0.111	1.00
nitrate*sieve size	-1.370	-0.685	0.785	-0.87	0.543	1.00
nitrate*binder	3.430	1.715	0.785	2.18	0.273	1.00
sieve size*binder	-0.720	-0.360	0.785	-0.46	0.726	1.00

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
2.22032	98.54%	89.75%	6.25%

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	6	331.612	55.269	11.21	0.225
Linear	3	303.291	101.097	20.51	0.161
nitrate	1	136.786	136.786	27.75	0.119
sieve size	1	7.373	7.373	1.50	0.436
binder	1	159.133	159.133	32.28	0.111
2-Way Interactions	3	28.320	9.440	1.91	0.478
nitrate*sieve size	1	3.754	3.754	0.76	0.543
nitrate*binder	1	23.530	23.530	4.77	0.273
sieve size*binder	1	1.037	1.037	0.21	0.726
Error	1	4.930	4.930		
Total	7	336.542			

Regression Equation in Uncoded Units

speed = 10.290 + 4.135 nitrate + 0.960 sieve size + 4.460 binder - 0.685 nitrate*sieve size + 1.715 nitrate*binder - 0.360 sieve size*binder

Figure 4: Factorial regression results. Factor A='nitrate'; to indicate if the KNO3 was in its dissolved state when the other ingredients were added, Factor B ='sieve size' and Factor C='binder'. The response variable was the speed of the cannonball.

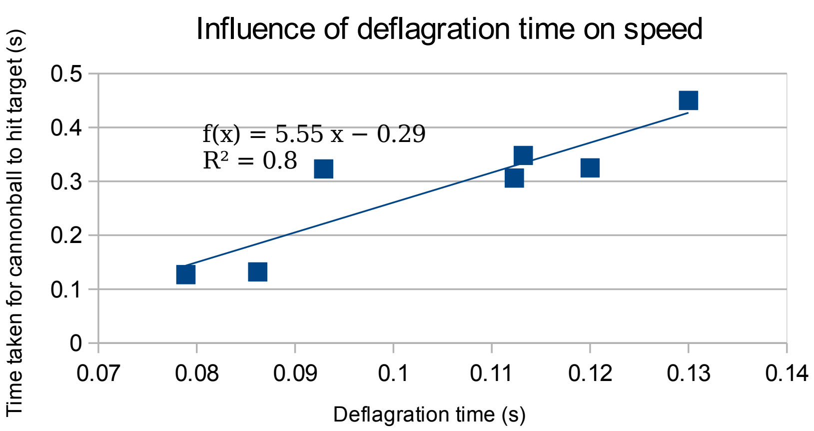

Figure 5: The effect of deflagration time on cannonball speed.

The results of the frequency versus amplitude for the gunpowder batches as analyzed by Audacity® is shown in Figure 6 below.

Frequency (H	Expt.1	Expt.2	Expt.3	Expt.4	Expt 5	Expt 6	Expt 7	Expt 8
43.066406	-11.723367	-7.511762	-4.576472	-6.610893	-9.848941	-25.032097	-21.700592	-7.642466
86.132812	-12.334341	-9.436401	-5.126819	-8.832101	-13.474888	-24.967012	-21.348927	-12.147734
129.199219	-14.566354	-10.504313	-7.58379	-10.923302	-16.712112	-23.377432	-22.524561	-15.388035
172.265625	-12.301252	-12.14015	-9.849981	-12.695639	-16.646042	-23.066139	-21.892683	-17.461365
215.332031	-12.437091	-10.077859	-9.13145	-9.54162	-17.934101	-21.805328	-22.887285	-15.882924
258.398438	-15.199479	-10.105246	-8.02489	-10.28075	-17.07542	-21.53129	-21.787886	-15.584252
301.464844	-15.461659	-9.985828	-7.998374	-10.106787	-13.194092	-24.981522	-20.733236	-16.819046
344.53125	-13.642993	-10.306662	-8.095852	-9.951799	-14.211355	-21.685097	-20.421597	-15.118856
387.597656	-12.821648	-9.997329	-8.947216	-7.852701	-15.924209	-22.354095	-20.56352	-15.125585
430.664062	-14.423783	-10.444263	-10.062783	-7.815333	-15.324344	-23.772257	-20.483927	-17.115383
473.730469	-15.443414	-12.202491	-9.906638	-10.054285	-14.129086	-20.283237	-22.431658	-16.670933
516.796875	-14.227777	-13.125048	-11.548401	-11.463683	-16.312057	-22.742161	-23.756481	-17.053543
559.863281	-13.015425	-13.775378	-11.304671	-11.667875	-19.432091	-24.548824	-24.365326	-17.316328
602.929688	-16.04237	-13.963279	-12.06835	-11.733783	-19.33827	-25.773077	-27.200062	-15.865322
645.996094	-17.087158	-13.03447	-12.40457	-12.392513	-19.121805	-27.042692	-28.000038	-19.254187
689.0625	-18.880367	-13.981901	-12.261893	-12.937774	-22.197638	-26.207628	-25.371836	-19.84495
732.128906	-17.437328	-13.208603	-14.368694	-12.78236	-22.544594	-28.195862	-26.589193	-19.528858
775.195312	-16.754061	-14.172621	-14.616064	-15.175087	-21.522007	-28.668076	-28.855776	-20.353466
818.261719	-17.667246	-17.086649	-12.82585	-15.239282	-21.736237	-26.182842	-26.273155	-20.16115
861.328125	-20.117537	-15.516188	-13.053839	-13.758284	-22.57173	-29.131268	-25.503424	-20.100437
904.394531	-20.201151	-15.018701	-14.563043	-13.949981	-24.103312	-29.311031	-28.515072	-21.67627
947.460938	-20.859592	-14.131426	-15.409685	-15.23133	-23.707123	-28.038149	-29.243668	-21.255693
990.527344	-20.847086	-15.254448	-15.847516	-16.89444	-25.269253	-32.243046	-29.811047	-23.449997
1033.59375	-22.834221	-17.111032	-15.301554	-17.507822	-26.948999	-33.162762	-32.07346	-27.764608

Figure 6: The amplitude of explosion across the frequency range 43 Hz to 1034 Hz, recorded by the Audacity software for the 8 gunpowder batches.

The gunpowder batches could be compared using the absolute values of the decibel levels. However, in order for that to happen, the microphone would have needed to be a fixed distance from the cannon. Since this was not part of the experimental setup, the results from Figure 6 were normalized to an amplitude of -1 dB at 43.066 Hz, so as to enable batch-to-batch comparison. The results are presented in Figure 7 below.

Frequency (H	Expt.1	Expt.2	Expt.3	Expt.4	Expt 5	Expt 6	Expt 7	Expt 8
43.066406	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
86.132812	-1.05	-1.26	-1.12	-1.34	-1.37	-1.00	-.98	-1.59
129.199219	-1.24	-1.40	-1.66	-1.65	-1.70	-.93	-1.04	-2.01
172.265625	-1.05	-1.62	-2.15	-1.92	-1.69	-.92	-1.01	-2.28
215.332031	-1.06	-1.34	-2.00	-1.44	-1.82	-.87	-1.05	-2.08
258.398438	-1.30	-1.35	-1.75	-1.56	-1.73	-.86	-1.00	-2.04
301.464844	-1.32	-1.33	-1.75	-1.53	-1.34	-1.00	-.96	-2.20
344.53125	-1.16	-1.37	-1.77	-1.51	-1.44	-.87	-.94	-1.98
387.597656	-1.09	-1.33	-1.96	-1.19	-1.62	-.89	-.95	-1.98
430.664062	-1.23	-1.39	-2.20	-1.18	-1.56	-.95	-.94	-2.24
473.730469	-1.32	-1.62	-2.16	-1.52	-1.43	-.81	-1.03	-2.18
516.796875	-1.21	-1.75	-2.52	-1.73	-1.66	-.91	-1.09	-2.23
559.863281	-1.11	-1.83	-2.47	-1.76	-1.97	-.98	-1.12	-2.27
602.929688	-1.37	-1.86	-2.64	-1.77	-1.96	-1.03	-1.25	-2.08
645.996094	-1.46	-1.74	-2.71	-1.87	-1.94	-1.08	-1.29	-2.52
689.0625	-1.61	-1.86	-2.68	-1.96	-2.25	-1.05	-1.17	-2.60
732.128906	-1.49	-1.76	-3.14	-1.93	-2.29	-1.13	-1.23	-2.56
775.195312	-1.43	-1.89	-3.19	-2.30	-2.19	-1.15	-1.33	-2.66
818.261719	-1.51	-2.27	-2.80	-2.31	-2.21	-1.05	-1.21	-2.64
861.328125	-1.72	-2.07	-2.85	-2.08	-2.29	-1.16	-1.18	-2.63
904.394531	-1.72	-2.00	-3.18	-2.11	-2.45	-1.17	-1.31	-2.84
947.460938	-1.78	-1.88	-3.37	-2.30	-2.41	-1.12	-1.35	-2.78
990.527344	-1.78	-2.03	-3.46	-2.56	-2.57	-1.29	-1.37	-3.07
1033.59375	-1.95	-2.28	-3.34	-2.65	-2.74	-1.32	-1.48	-3.63

Figure 7: Normalized Frequency-amplitude data for the 8 gunpowder batches.

A graphical representation of the results from Figure 7 is presented in Figure 8 below.

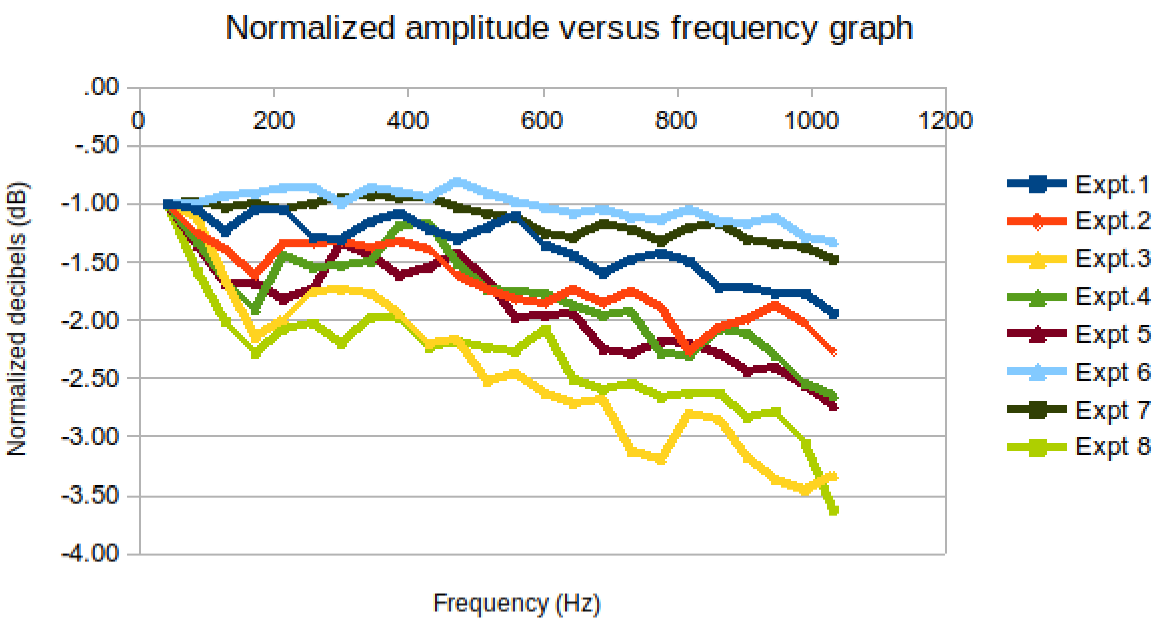

Figure 8: Normalized amplitude versus selected frequency graphs for the 8 batches of gunpowder.

Discussion

The cannon was a scaled down version of a 3.67 inch caliber, 5 feet, M1841 6-pounder bronze field gun capable of firing a 2.8 Kg shot with a charge of 0.6 Kg. Since we used a PVC pipe instead of bronze, we erred on the side of safety and used a 1 inch caliber, 9.5 inch cannon with a 65 g cannonball and a 5 g charge. Therefore, while not being an exact scaled down replica, the objectives of safety and measurable/discriminable speed were met during preliminary experiments.

Gunpowder is classified as a low-yield explosive, which typically deflagrates, thus making it a good propellant. It can generate enough pressure to force the projectile from the muzzle at high speed, but usually not enough force to rupture the barrel. The rate of ignition propagation from grain to grain of corned (slightly wetted, pressed with a hydraulic press, let dry, crushed and screened) black powder is over two orders of magnitude faster than the burning rate within a grain of black powder. While we use the term 'detonation force' or 'detonation power' in this manuscript, we did not actually measure the initial shock-wave velocity and determine it to be supersonic. Therefore, our use of the term, 'detonation' is metaphoric and should be taken to imply the ratio of the relative time of the inter-grain combustion propagation to the intra-grain burning rate; the phenomenon changing from deflagration to detonation as this ratio decreases (primarily by increasing the denominator).

Effect of molecular dispersion of ingredients

The KNO_3 was in its dissolved molecular state when it was mixed with the charcoal and the sulfur in experiments 1 through 4. This necessarily implied that there was more intimate mixing of the three ingredients. The average speed for the cannonball was 14.7 m/s for experiments 1 through 4. On the other hand, for experiments 5 through 8, the KNO_3 was mixed as a powdered solid (particles < 0.85 mm, sieve size #20) with the other ingredients, therefore the magnitude of molecular intimate mixing was significantly lesser than that for experiments 1 through 4. This may, in part, be why the average speed of the cannonball for experiments 5 through 8 (6.0 m/s) was significantly lesser than the average speed for experiments 1 through 4.

The average cannonball speed obtained from batches 1 and 3 (8.2 m/s) was compared with that obtained with batches 5 and 6 (8.7 m/s). The speeds were comparable despite the fact that batches 5 and 6 were formulated with binder while batches 1 and 3 were not. This data illustrated the importance of intimate molecular mixing between the ingredients. Batches 1 and 3 were formulated with dissolved KNO_3, whereas batches 5 and 6 were formulated with powdered KNO_3. It was reasonable to conclude that the three ingredients; KNO_3, C and S, were uniformly distributed across all the particles of batches 1 and 3 even though the batch was prepared without binder. Therefore, even though these batches deflagrated due to the unhindered propagation of combustion, the rate of this deflagration was comparable to the (weak) detonative force for batches 5 and 6. The detonative force for batches 5 and 6, manufactured with binder was weak because, even though the initial deflagrative combustion propagation was hindered due to the presence of binder, the subsequent detonation was desynchronized across the number of granules; on account of the non-uniform mixing of ingredients within each granule.

Effect of particle size distribution

For experiments 5 and 6 with binder, the speed of the cannonball was inversely proportional to the fraction of the gunpowder that passed through sieve # 16, although the effect was not significant. A similar effect was observed for experiments 7 and 8, prepared without binder, where the speed of the cannonball was also found to be inversely proportional to the fraction of the gunpowder that passed through sieve # 16. This phenomenon could be interpreted to mean that a narrower size distribution of the corned gunpowder particles was directly proportional to its explosive power, and/or that a larger particle size was required to yield a larger explosive power. However, this phenomenon was not evident in batches 2 and 4 that were prepared using dissolved KNO_3 with binder added (see below for further explanation).

Effect of presence of binder

The presence of binder in batches 2 and 4 significantly increased the explosive force of the gunpowder that was prepared from dissolved KNO_3, when compared with the speed of the cannonball in batches 1 and 3, that did not contain binder. This effect was observed despite the fact that batches 1 through 4 probably consisted of a similar distribution of the three ingredients across all the particles. It can thus be speculated that contact points between the particles for batches 1 and 3 significantly increased deflagration. This was corroborated from an observation of batches 7 and 8, both of which were formulated without a binder. Since the average particle size of batch 7 was less than that of batch 8 - also evidenced in the percent of particles that passed through the #16 sieve - there were more contact points between the particles of batch 7, than those between particles of batch 8. Hence the deflagration was greater for batch 7 than that for batch 8. Consequently, the velocity of the cannon ball for batch 7 was not measurable (and taken to be an order of magnitude lesser than) the velocity of the cannon ball for batch 8. The presence of the binder may hence act to decrease the ‘fire spread’ from the ignition front; much like ‘fire blocking wood stops’ act to retard the spread of a fire in a home. The net result is that; only when the majority of the particles reach a critical temperature do they combust; more-or-less; simultaneously, thereby causing a detonative supersonic shock-wave; rather than a heat-induced propagative combustion at subsonic speeds; i.e. a deflagration. This also implied that the effect of particle size distribution should be lesser on the detonative power of the gunpowder prepared with a binder than that prepared without one. This indeed was observed with our set of experimental conditions. Batches 2 and 4 exhibited comparable velocities even though the weight percent of particles that passed through the #16 sieve was dis-similar (26.1% and 38.5% respectively). Similarly, batches 5 and 6 exhibited comparable velocities even though the weight percent of particles that passed through the #16 sieve was dis-similar (10.9% and 40.0% respectively).

The legacy practice of ‘corning’, *viz.* the enlargement of the particle size of finely ground black powder; and then subsequently fractionated into different particle size distributions improved its combustion and adapted it to different applications depending on the burn rate. Black powder is sold as several grades depending on particle size. Sporting grades 1FG, 2FG, 3FG and 4FG have granule ranges of 1.68-1.19 mm, 1.19-0.59 mm, 0.84-0.29 mm, and 0.42-0.15 mm respectively. The results from our experimental regime suggest that if the black powder can be ground to a fine enough size such that a uniform distribution of the three ingredients is obtained across all the particle sizes, it may be that the explosive power is then not as dependent on the polydispersity and differentiation in the average particle size of the corned product; as it is on the type of binder and its concentration. We cannot however, predict that other experimental regimes will produce similar results.

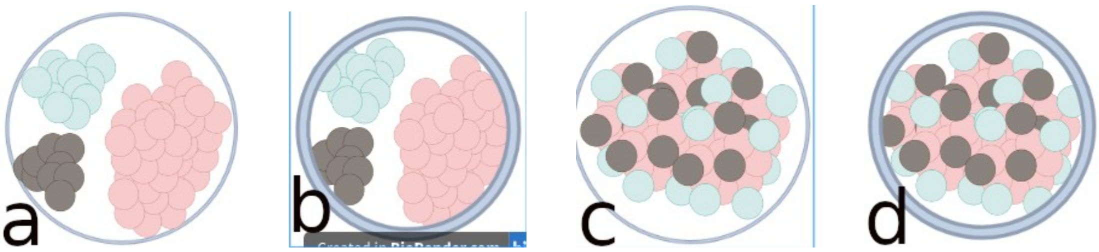

Figure 9: Cartoon depiction of an idealized spherical black powder particle. a. KNO_3 is not dissolved in water during manufacture, no binder added. b. KNO_3 is not dissolved in water during manufacture, binder added. c: KNO_3 is dissolved in water during manufacture, no binder added. d: KNO_3 is dissolved in water during manufacture, binder added. Key: Pink = KNO_3, Brown = Charcoal, Blue = Sulfur.

Figure 10 below shows the classification of batches based on the discussion above. The batches are classified into four quadrants as follows: Quadrant I, top right: Batches 1 and 3. Increased deflagration time and synchronous combustion. Quadrant II, top left: Batches 2 and 4. Decreased deflagration time and synchronous combustion. Quadrant III, bottom left: Batches 5 and 6. Decreased deflagration time and asynchronous combustion. Quadrant IV, bottom right: Batches 7 and 8. Increased deflagration time and asynchronous combustion.

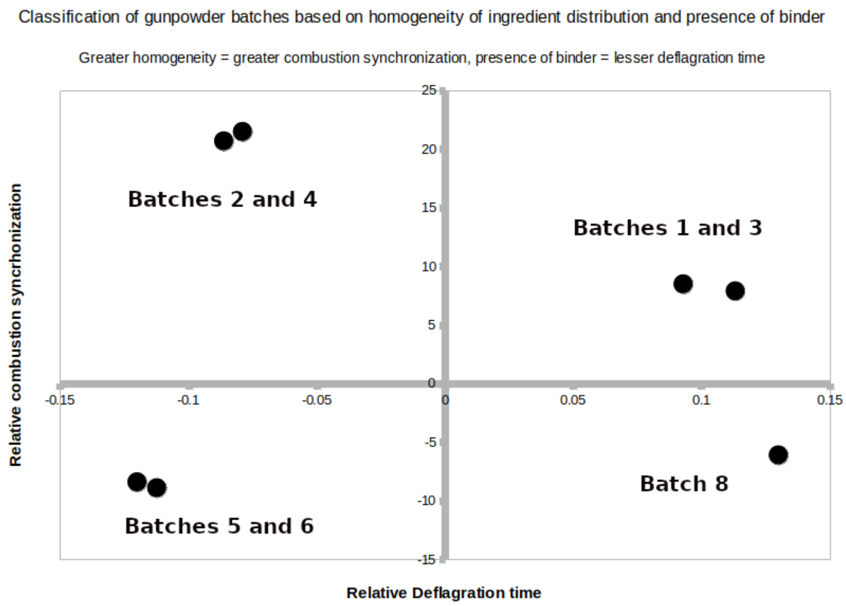

Figure 10: Classification of gunpowder batches in quadrants based on the presence of binder (batches 2, 4, 5 and 6 have binder present in the formulation) and the homogeneity of distribution of ingredients (batches 1 through 4 have greater homogeneity). Data is derived from Table 2 with the appropriate sign (negative or positive) inserted for speed and deflagration time. Deflagration time is set to negative and positive in the presence and absence of binder respectively. The speed of the cannonball; taken to be proportional to the relative combustion synchronization; is set to negative and positive for dry and wet gunpowder batches respectively.

Figure 10 is a graphical representation of the mechanisms of deflagration and combustion discussed above. Batches 1 and 3 are wet batches prepared with dissolved KNO_3 but contain no binder. Therefore, the combustion of each grain is synchronous but the gunpowder as a solid mass undergoes greater deflagration due to no binder being present and the grains contacting each other. Batches 2 and 4 are wet batches prepared with dissolved KNO_3 and contain binder. Therefore, not only is the combustion of each grain synchronous, but the combustion of the gunpowder solid mass is as well. This is because the solid mass undergoes lesser (symbolized by negative) deflagration due to the majority of grains being unable to contact each other due to the binder coating. Batches 5 and 6 are dry batches with lesser homogeneity of ingredients and hence exhibit both inter- and intra-grain combustion asynchronization (negative combustion synchronization). However, their solid mass does undergo lesser (negative) deflagration due to the binder coating. Batches 7 and 8 (batch 7 not shown), are the worst performing batches in the fourth quadrant because they are dry batches that contain no binder. As can be seen from the figure, batches 2 and 4, in quadrant II are the best performing gunpowder batches because they exhibit both combustion synchronization and a lesser relative deflagration time.

Amplitude-frequency graphs versus overpressure-time graphs

From an examination of the raw text data, the greatest amplitude discrimination among the batches occurred between 43.066 Hz and 1033.59 Hz. Therefore, this region of the frequency spectrum was chosen to search for patterns in amplitude that could be predictive of the deflagration time for that gunpowder batch. As a first-approximation, a greater drop-off of amplitude with increasing frequency may reasonably be inferred as a greater combustion simultaneity of all the grains of the gunpowder.

The general shape of the graphs in Figure 8 is reminiscent of the overpressure versus time shock-blast pulses generated by high-explosive detonations (3 - 6). The initial negative slopes; $\Delta dB_{(0\text{-}200)}$ may represent the rapid release of energy; exemplified by a supersonic detonation blast; signified by a significant reduction in amplitude at incrementally increasing frequencies. This occurs in the range of 0 Hz to 200 Hz as seen in Figure 8. In the next ‘recovery’ phase, the amplitude then increases again with incremental increase in frequency from 200 to 400 Hz ($\Delta dB_{(200\text{-}400)}$) before decreasing at higher frequencies. This may represent either a secondary detonation or the remnant of a pulsed shock wave front that propagates across frequencies.

An examination of Figure 8 indicated that the initial decrease in amplitude from 0 to 200 Hz was absent in gunpowder lots 6 and 7; and minimal in batch 1; consistent with these lots presenting the least cannonball speeds. Batch 8 did exhibit one of the largest initial decreases in amplitude, but the subsequent recovery from 200 to 400 Hz was minimal. As a first approximation, it appeared from an empirical standpoint that the deflagration time may be inversely proportional to the overpressure; i.e. the initial decrease in amplitude; as well as being inversely proportional to the ratio of recovery to initial decrease [$\Delta dB_{(0\text{-}200)}$ / $\Delta dB_{(200\text{-}400)}$]. Furthermore, the latter [$\Delta dB_{(0\text{-}200)}$ / $\Delta dB_{(200\text{-}400)}$], would probably need to be normalized to the absolute initial decrease in amplitude, in order to be comparable across gunpowder batches. A final point to be considered was that the initial amplitude drop would also need to be normalized across a constant frequency range (43.06 Hz to 172.3 Hz) in order for the normalization algorithm to work. The results of these calculations are presented in Table 3. As an example, for experiment # 1,

$$[(\Delta dB_{(0\text{-}200)}) / (\Delta dB_{(200\text{-}400)})\hat{}\,\Delta dB_{(0\text{-}200)})] \text{ is calculated as: } (0.826)/(1.05^{0.826}) = 0.793$$

Table 3: Calculation of the frequency-amplitude parameter from normalized frequency-amplitude curves for the 8 batches of gunpowder

Experiment #	$\Delta dB_{(0-200)}$ (Frequency range, Hz)	$\Delta dB_{(0-200)}$ (normalized across 172.3-43.06)	Recovery amplitude $\Delta dB_{(200-400)}$	$[(\Delta dB_{(0-200)}) / (\Delta dB_{(200-400)})^{\wedge}\Delta dB_{(0-200)})]$
1	1.24 (129.2-43.06)	0.826	1.05	0.793
2	1.62 (172.3-43.06)	1.62	1.33	1.021
3	2.15 (172.3-43.06)	2.15	1.75	0.645
4	1.92 (172.3-43.06)	1.92	1.18	1.397
5	1.70 (129.2-43.06)	1.133	1.34	0.813
6	0	0	NA	0
7	0	0	NA	0
8	2.28 (172.3-43.06)	2.28	1.98	0.480

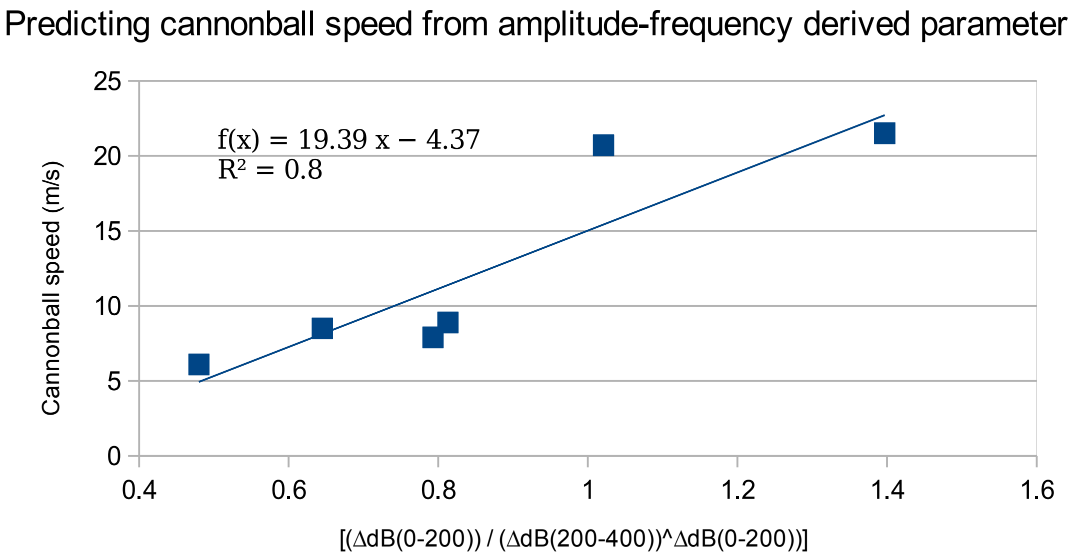

Figure 11: Prediction of cannonball speed from the data in Table 3. $[(\Delta dB_{(0-200)}) / (\Delta dB_{(200-400)})^{\wedge}\Delta dB_{(0-200)})]$. Experiments 6 and 7 are not included in the graph.

Limitations

We could not keep the binder concentration constant for those batches in which binder was present. This is because we wanted the binder to be distributed uniformly throughout the mixed ingredients, hence it had to be dissolved in water prior to mixing. Since different batches required different amounts of water to attain the dough-like consistency, the binder concentration was different for different batches. The binder concentrations were consequently 1.2%, 1.6%, 1.7% and 2.6% for gunpowder batches 2, 4, 5 and 6 respectively. However, since the DOE called for the absolute absence or presence of gunpowder; and even a 116% increase in the percentage of binder (batches 2 and 6) could not alter the general observed trend; this binder range could be assumed to have a non-significant effect on the response variable. It could be that above a certain concentration, all, or the majority of the individual grains of gunpowder were already coated, such that further increase in binder concentration would be ineffective; although we cannot provide any experimental evidence of such a saturation phenomenon.

We did not measure the residual water content of the gunpowder batches, therefore we do not know what effect - if any - this variable had on our results. Gunpowder is known to be hygroscopic, therefore, each manufactured batch was tested and used within 24 hours of manufacture.

While the amplitude-frequency parameter explained 80% of the variation in the speed of the cannonball (Figure 11), it was empirically calculated without any ‘first principles’ explanation. Although the slope and extent of the initial dB amplitude across increasing frequencies can be logically assumed to parallel the overpressure-shockwave graphs of explosive detonations (3-6), we are unsure of what the ‘recovery phase’ in the frequency range of 200 Hz to 400 Hz physically signifies. We speculate this to be either a secondary detonation or a pulsed acoustic wave propagating across those frequencies that is correlated with the detonation efficiency. Nevertheless, this acoustic ‘recovery’ phenomenon – relative to the initial decrease in dB amplitude – determined the speed of the cannonball. Future work may succeed in explaining the physical significance of this phenomenon.

Conclusion

The detonative power of gunpowder, defined by the speed of the cannonball; could be measured by using a free, open-source multi-track audio editor and recorder software; Audacity®. ~90% (Figure 4, R-sq(adj)) of the variation in the speed of the cannonball could be explained by two principal factors. These were: 1] the homogeneity of distribution of all the three ingredients, within and across all the particles constituting the batch. The more uniformly the three ingredients were distributed within and across all the particles, the greater the detonative power, and 2] the deflagration time; which in turn was dependent on the presence of binder in the formulation; the larger the efficiency with with the binder acted as a ‘fire block’, the lesser the asynchronous deflagrative subsonic propagation of the combustion front through the granules, and consequently, the greater the synchronous intra and inter grain supersonic detonative power. These two dependent variables presented with the lowest p-values (< 0.12) in the DOE results, although neither was statistically significant in our experimental design.

The mechanisms that yield the greatest detonative force, proposed in this manuscript, i.e. those of achieving the greatest synchronous supersonic combustion and the least deflagrative subsonic propagation of the combustion front, were validated by the clustering of similarly behaving gunpowder batches in the four quadrants of an ingredient homogeneity - deflagration time plot. They were also validated by recognizing that the amplitude-frequency plot could be interpreted similar to standard overpressure-time plots. Consequently, the amplitude-frequency derived parameter was correlated with the cannonball speed; and hence, with the detonative force of the gunpowder.

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