Supporting Information for

Evolution of Medieval Gunpowder: Thermodynamic and Combustion Analysis

Tessy S. Ritchie[1], Kathleen E. Riegner[2], Robert J. Seals[3], Clifford J. Rogers[3], Dawn E. Riegner[1]*

[1]United States Military Academy, Department of Chemistry and Life Science, West Point, NY 10996

[2]Stevens Institute of Technology, Department of Chemical Engineering & Materials Science, Hoboken, NJ 07030

[3]United States Military Academy, Department of History, West Point, NY 10996

*dawn.riegner@westpoint.edu

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1. Bomb Calorimetry

Methods of Instrumental Analysis

A Parr Instruments oxygen bomb calorimeter and Parr fuse wire with a heat of combustion of 2.3 cal/cm were used to determine the heat of combustion of each recipe. Untreated cotton string was used in the ignition process. A thermistor and a MicroLab interface were used to record the temperature change during the combustion process.

The bomb calorimeter was calibrated at the beginning of each week of testing. To calibrate the bomb, a Parr benzoic acid pellet, standardized for bomb calorimetry, with heat of combustion of 6318 cal/g, was used. Seven cm of wire was connected across the electrodes and 13 cm of untreated cotton string was tied to the center of the wire and coiled into the cup. The pre-weighed pellet was placed on the string, in the cup, and the bomb was closed. Before igniting, the bomb atmosphere was cycled with oxygen, then charged with oxygen to approximately 20 atm. The charged bomb was placed in a 2.00 L tap water bath in the bomb calorimeter. The water was stirred until the thermistor read a steady temperature for at least 30 seconds, then the bomb was ignited. The changing temperature of the water was recorded until a steady temperature had been reached. The heat capacity (J/ºC) of the bomb calorimeter was calculated from the calibration with benzoic acid by using the following equation:

Equation S1 $$C = \frac{-nE+(9.6)(W)}{\Delta T}$$

Where:

n is moles of benzoic acid [moles], E is heat of combustion of benzoic acid [J/mole], W is length of remnant wire [cm], ΔT is change in temperature [ºC].

The same process was repeated for each gunpowder sample tested, and the change in temperature was confirmed by two different researchers' analysis of the thermistor data and averaged for each sample. Then the change in temperature was used to calculate the heat of combustion (J/g) for each gunpowder recipe with the following equation:

Equation S2 $$H = \frac{(C)(\Delta T)+(W)(9.6)}{m}$$

Where:

C is heat capacity of bomb calorimeter [J/ºC], ΔT is change in temperature [ºC], W is length of remnant wire [cm], m is mass of the original sample [g]. A Student's T-test was performed to determine if there were statistically significant differences whenever heats of combustion were compared.

Relative Reaction Rate Determination

The relative, instantaneous rates of reaction were also analyzed for each gunpowder recipe tested in the bomb calorimeter. Raw data from the first 100 seconds after ignition were analyzed. This allowed a linear line of best fit to be used to calculate the relative instantaneous rate of heat transfer (ºC/s) caused by the ignition of the gunpowder. The slopes of the lines of best fit were averaged for a minimum of three trials, giving relative rates of reaction across the recipes. These rates do not represent the true instantaneous rate of reaction because the thermistor measured the temperature change of the water in the calorimeter, not direct temperature change from the ignited gunpowder.

Data

Table S1. Summary of bomb calorimetry results

Recipe Name and Ratio (KNO_3:S_8:C)	Form and Additives (if any)	Heat of Combustion (kJ/g)	Relative Reaction Rate (°C/s) x 10^{-3}	Temperature Fluctuation
1-E 2:1:2	Serpentine	12.83 ± 0.40	4.10 ± 0.26	High
	Pressed with water	12.02 ± 0.37	3.20 ± 0.36	
	Corned with varnish	13.31 ± 0.69	4.68 ± 0.50	
4-C 10:1:10	Serpentine	12.40 ± 0.39	4.17 ± 0.51	High
	Pressed with water	13.08 ± 0.37	3.48 ± 0.61	
	Corned with varnish	11.37 ± 0.27	3.87 ± 0.60	
1-D 2:1:1	Serpentine	9.19 ± 0.06	2.93 ± 0.50	High
1-C 4:2:1	Serpentine	6.94 ± 0.36	2.13 ± 0.12	Medium
	Pressed with water	6.93 ± 0.26	2.23 ± 0.35	
	Corned with vinegar	5.70 ± 0.17	2.03 ± 0.23	
1-B 4.15:2.22:1	Serpentine	6.65 ± 0.23	2.37 ± 0.23	Medium
	Pressed with water	6.96 ± 0.12	2.30 ± 0.10	
2-A 5:2:1	Serpentine	6.49 ± 0.11	2.13 ± 0.23	Medium
	Pressed with water	6.39 ± 0.21	1.97 ± 0.15	
1-A 3.67:3:1	Serpentine	6.40 ± 0.79	2.05 ± 0.13	Medium
3-A 8:2:1	Serpentine	5.27 ± 0.86	1.74 ± 0.25	Low
	Corned with water	3.82 ± 0.13	1.33 ± 0.12	
	Corned with brandy - Additives: Camphor, Ammonium Chloride, SalPracticum	4.82 ± 0.12	1.33 ± 0.02	
4-B 15:2:3	Serpentine	5.10 ± 0.31	1.50 ± 0.27	Medium
	Pressed with water	4.36 ± 0.67	1.47 ± 0.25	
	Corned with water	4.94 ± 0.36	1.60 ± 0.10	
4-A 22:4:5	Serpentine	4.97 ± 0.18	1.63 ± 0.12	Medium
2-B 6:2:1	Serpentine	4.61 ± 0.05	1.45 ± 0.10	Medium
	Corned with vinegar	5.25 ± 0.34	1.67 ± 0.15	
2-C 7:2:1	Serpentine	4.49 ± 0.61	1.52 ± 0.26	Low
	Corned with brandy	5.15 ± 0.28	1.80 ± 0.00	
4-D 16:1:4	Serpentine	4.48 ± 0.08	1.57 ± 0.58	Low
	Pressed with water	3.93 ± 0.47	1.47 ± 0.58	
3-B 5:1:1	Serpentine	2.97 ± 0.24	1.17 ± 0.15	Low
	Serpentine - Additives: Camphor, Quicklime	3.37 ± 0.62	1.10 ± 0.58	

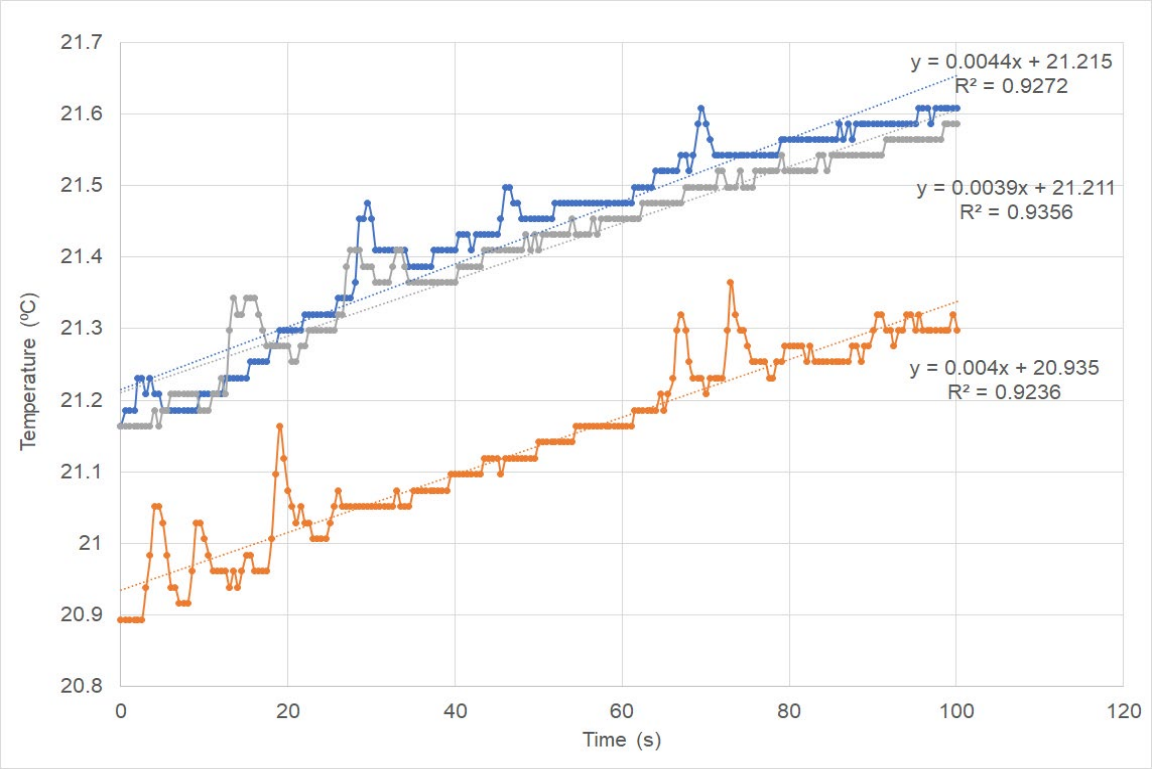

Figure S1a. 1-E serpentine reaction rate.

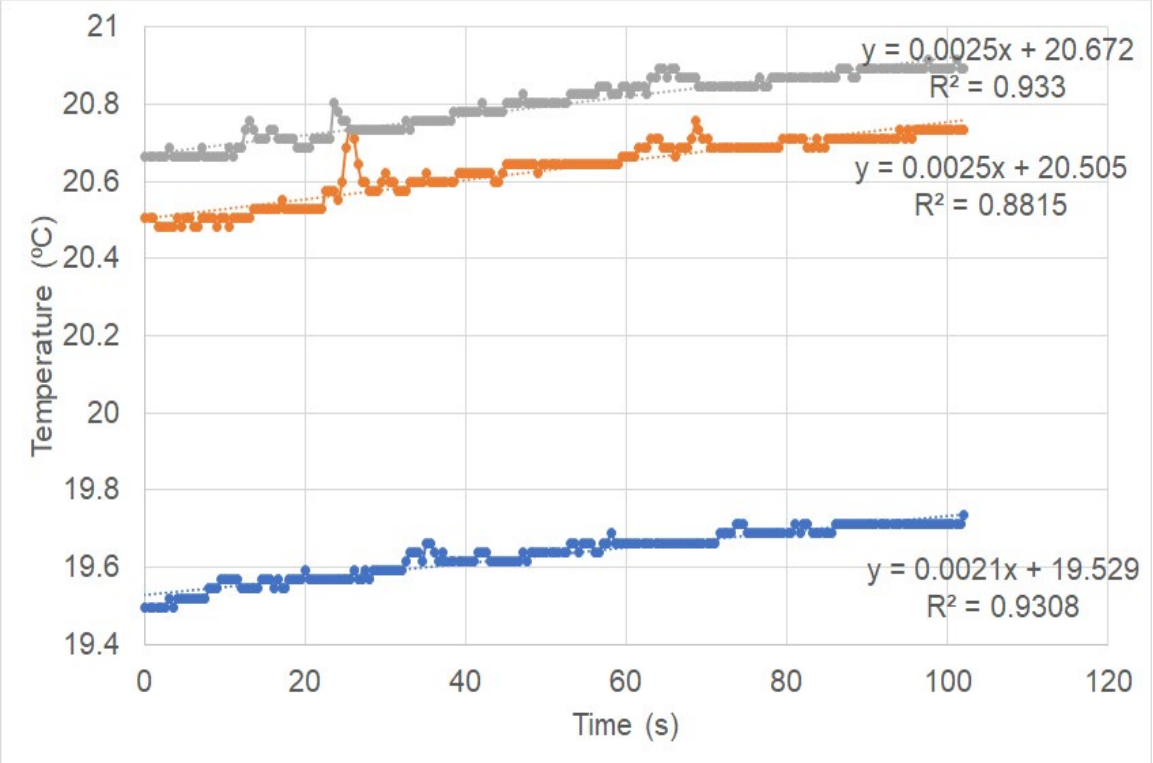

Figure S1b. 1-B serpentine reaction rate.

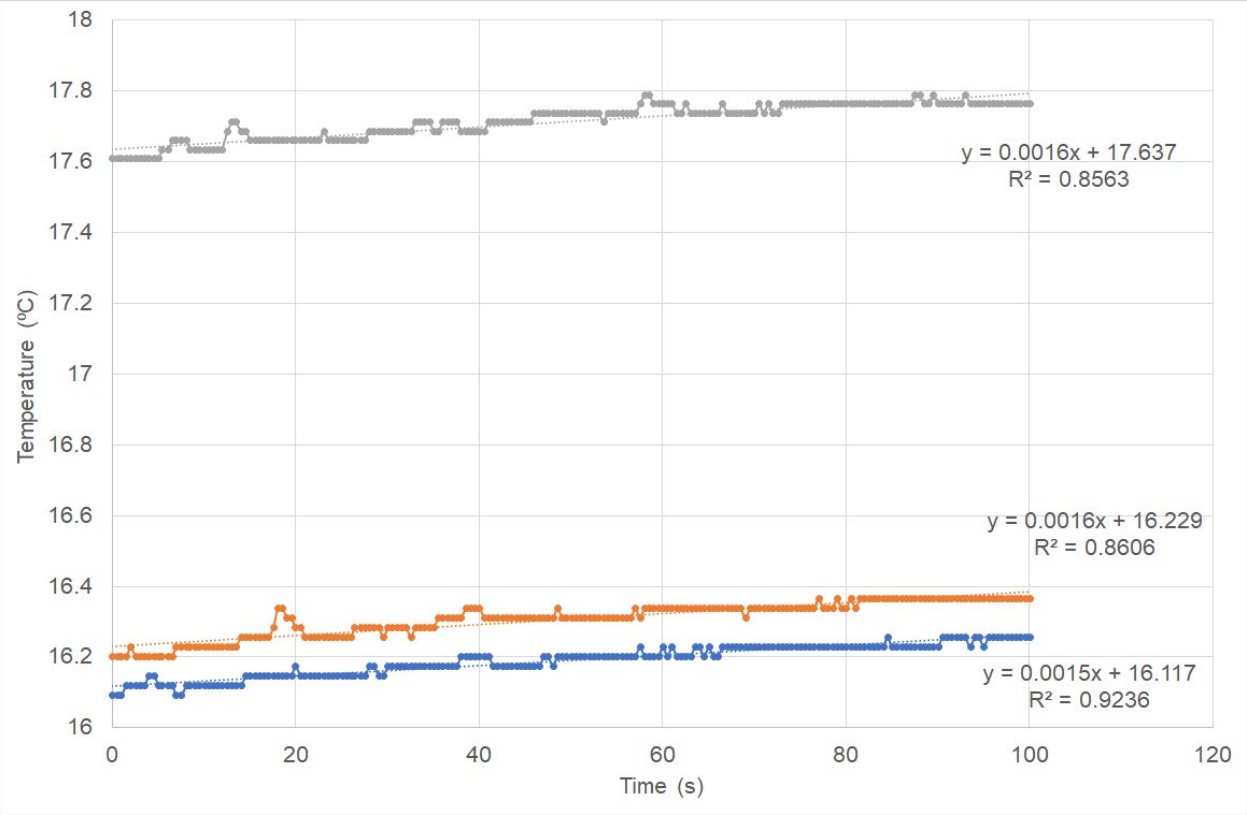

Figure S1c. 4-D serpentine reaction rate.

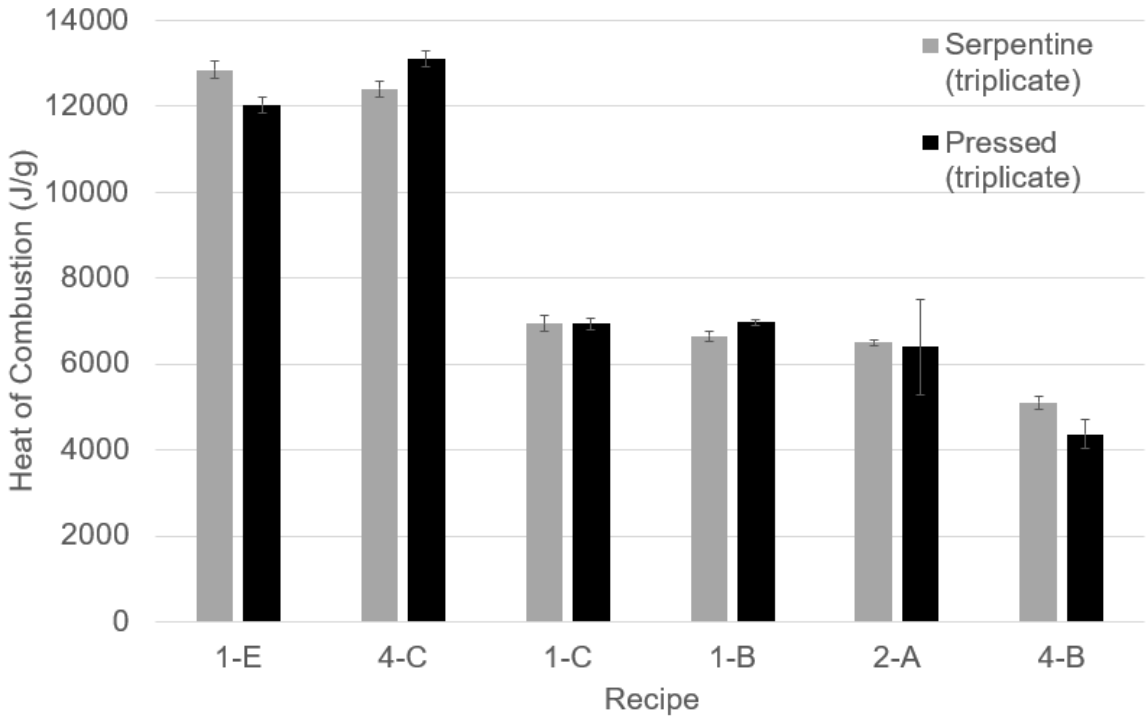

Figure S2 Serpentine vs Pressed.

2. Differential Scanning Calorimetry

Methods of Instrumental Analysis

Analysis of gunpowder mixtures and residues were conducted on TA Instruments 250 DSC series. Standard aluminum pans were prepared with samples ranging from 4.00 to 13.00 mg. The pans were then crimped before beginning analysis. A heat/cool/heat (H/C/H) cycle was used where the heating ramps were 10°C/min and the cooling ramp was 5°C/min. This allowed for analysis of the pre and propagative ignitions in the first heating cycle (25°C to 400°C), recrystallization (400°C to -50°C) and melting (-50°C to 400°C) of any remaining materials. The Discovery TA Trios software was used to determine the enthalpy of samples using a linear baseline model.

Data

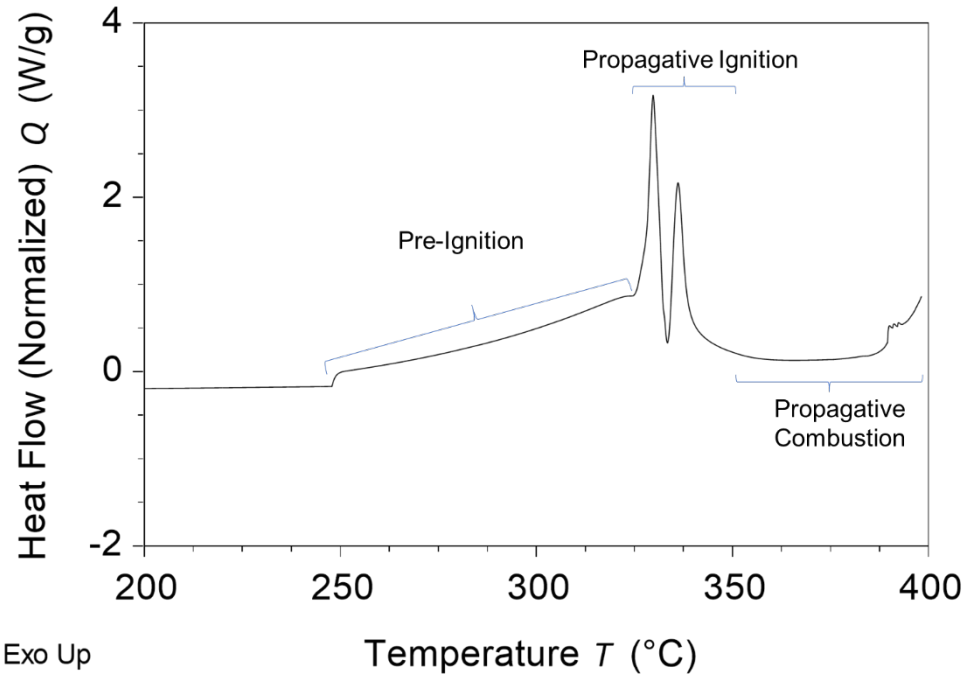

Figure S3 Example 1st heat cycle DSC of gunpowder showing pre-ignition, propagative ignition and propagative combustion (sometimes referred to as propagative reactions).

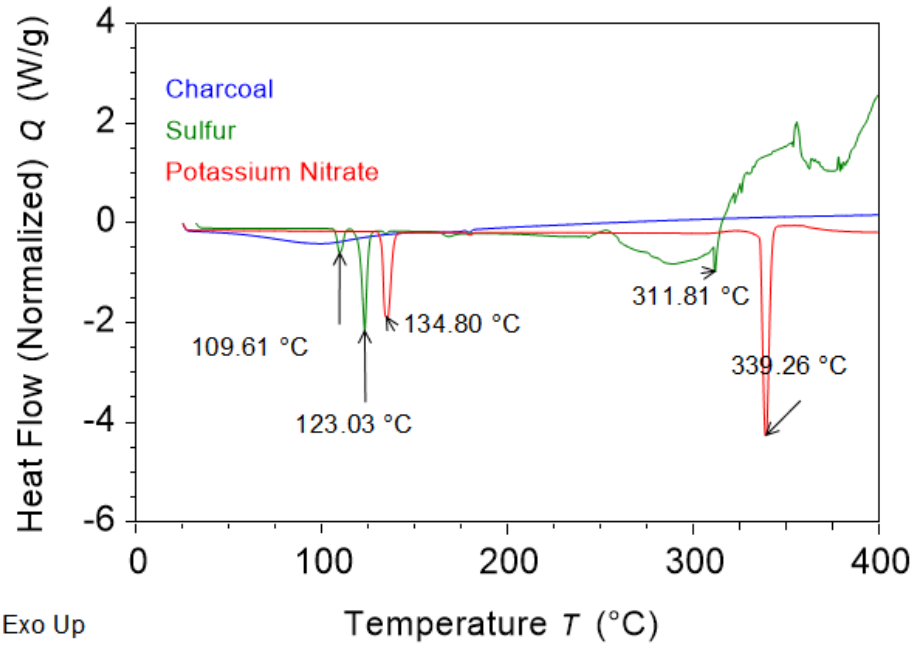

Figure S4a. DSC overlay of Sulfur, Charcoal and Potassium Nitrate. 1st heat shown, Heating ramp was 10°C/min. As reported in the literature, sulfur and KNO_3 exhibited melting points at 123.03°C and 339.26°C, respectively. The temperature ramp also allowed the visualization of KNO_3's rhombic to trigonal transition in the first heating cycle (134.80°C).

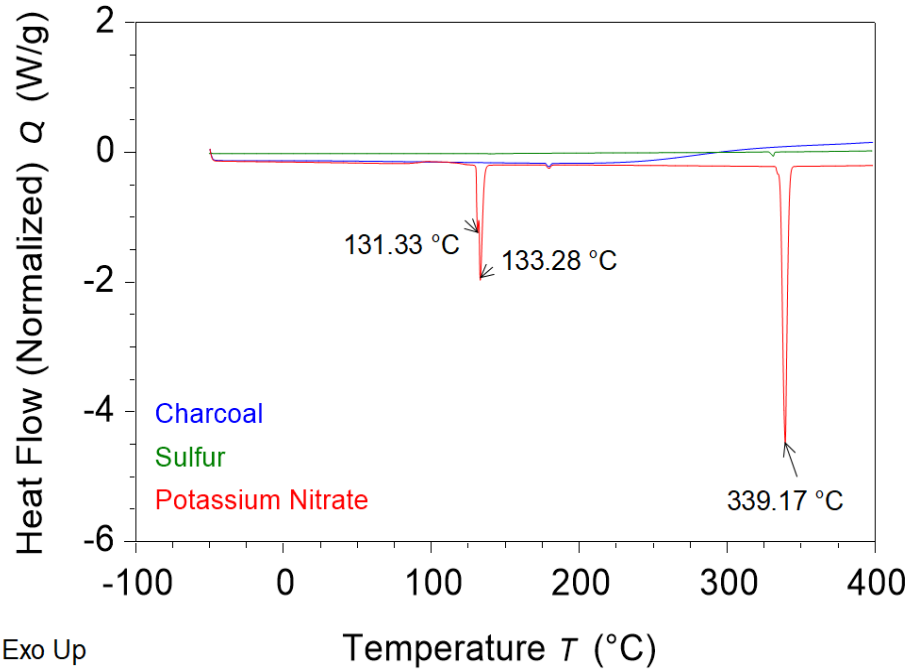

Figure S4b. DSC overlay of Sulfur, Charcoal and Potassium Nitrate. 2nd heat shown, Heating ramp was 10°C/min. Two distinct peaks appeared which likely captured the transformation between two known rhombic forms in KNO_3 (131.33°C, 133.28°C)

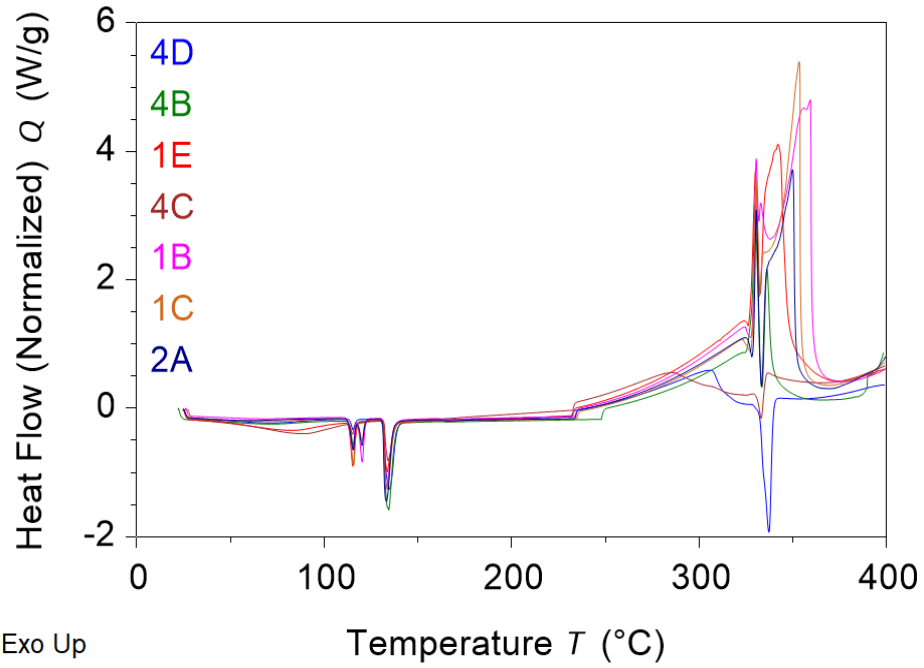

Figure S5a. DSC overlay of gunpowder recipes. 1st heat shown, Heating ramp was 10°C/min.

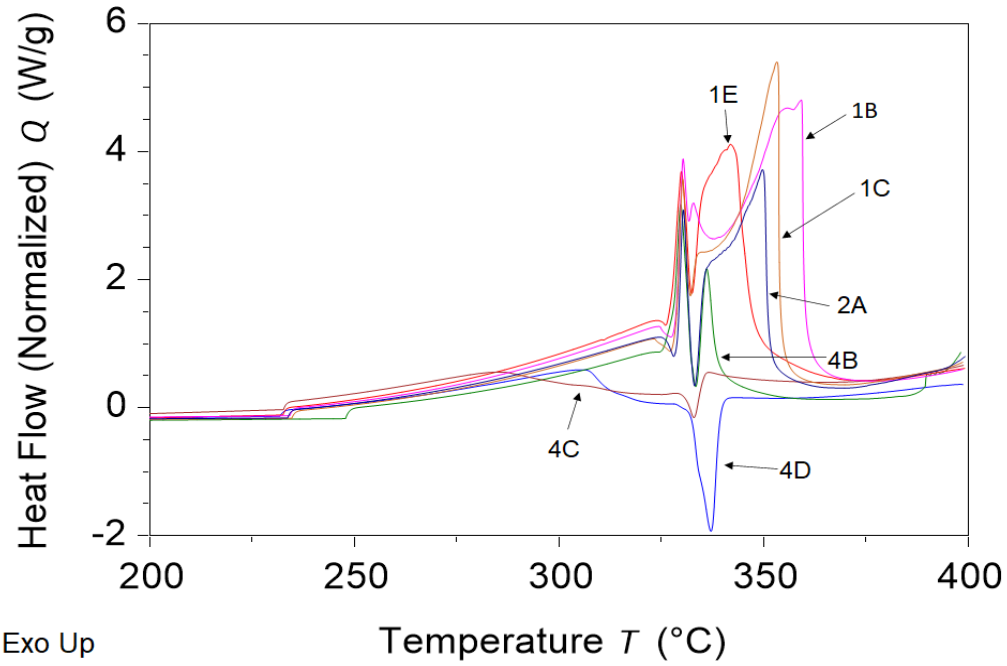

Figure S5b. DSC overlay of magnified region from Figure S5a. 1st heat shown, Heating ramp was 10°C/min zoomed in on the region where propagative ignition occurs.

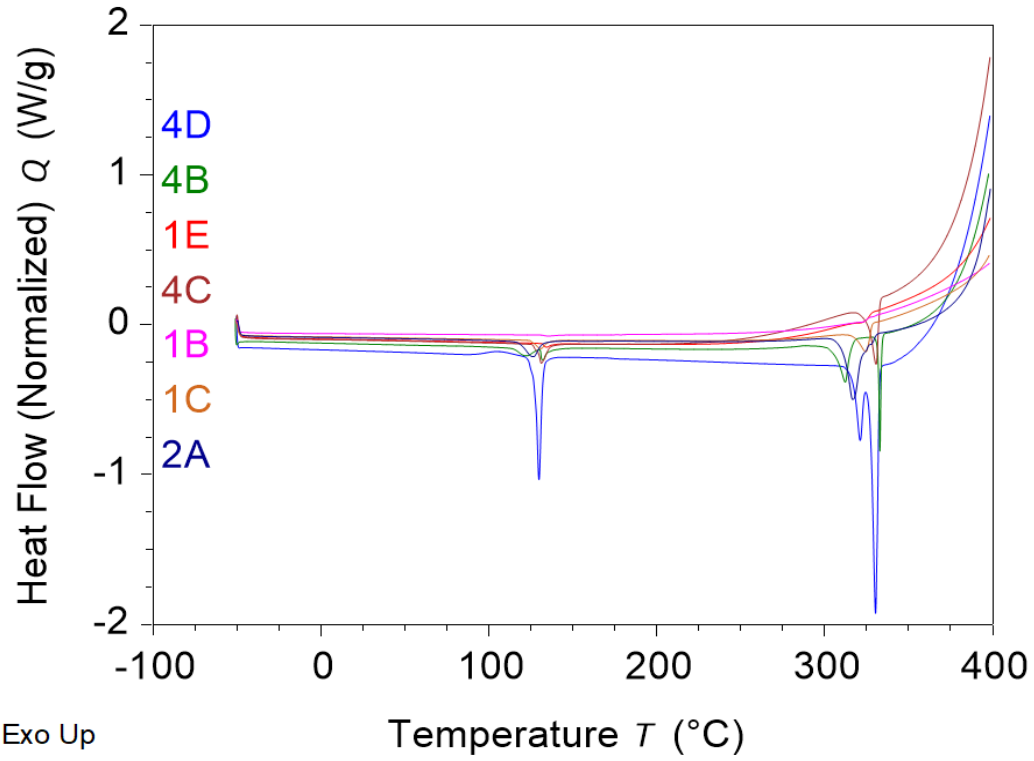

Figure S6a. DSC overlay of gunpowder recipes from Figure S5a. 2nd heat shown, Heating ramp was 10°C/min.

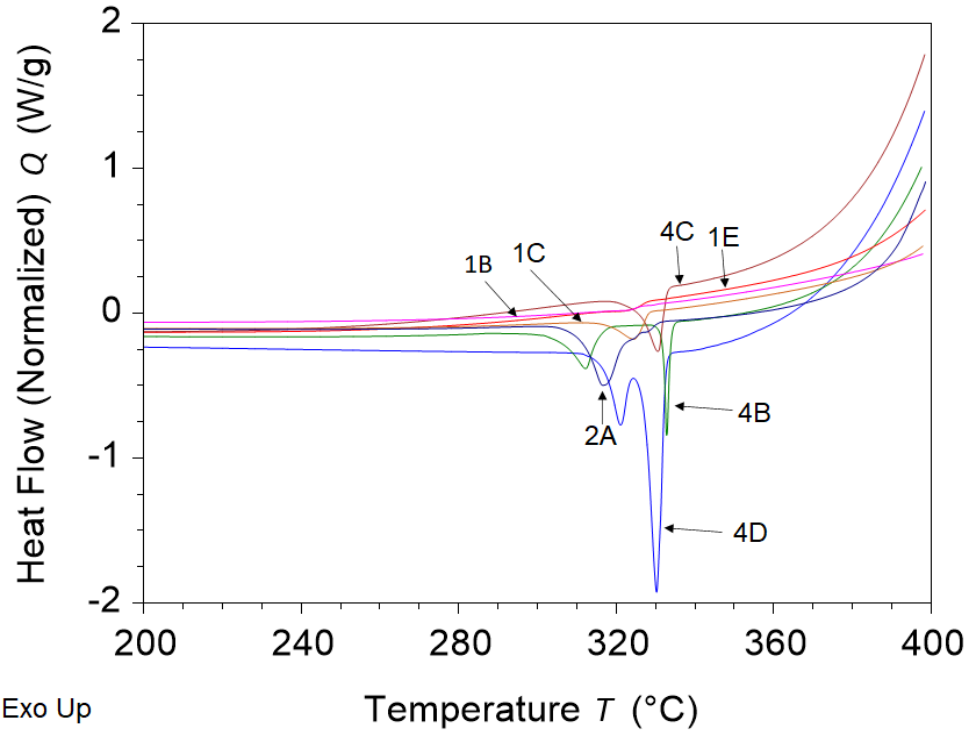

Figure S6b. DSC overlay of magnified region from Figure S6a. 2nd heat shown, Heating ramp was 10°C/min

3. Field Testing Data

Table S2. Summary of DSC cannon residue results

Sample	Cannon Residue (1^{st} Heat (J/g))	Bomb Residue (1^{st} Heat (J/g))	DSC "Residue" (2^{nd} Heat (J/g))	Cannonball Speeds m/sec
1-C-i	138.52 (exo)	60.077 (exo)	0.67818 (endo)	---
2-B-i	104.81 (exo)	7.4252 (exo)	0.20511 (endo)	45
3-A-i	---	37.293 (endo)	14.305 (endo)	97
3-A-ii	109.71 (exo)	39.703 (endo)	1.4597 (endo)	---