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CARBON BLACK VS CHARCOAL. INFLUENCE ON COMBUSTION PROPERTIES OF SELECTED PYROTECHNIC COMPOSITIONS

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Abstract: *Conventional black powder typically consists of charcoal, sulfur and potassium nitrate (KNO_3). The use of other carbon-based substances instead of charcoal has been less common. Following the development of time delay pyrotechnic compositions in this research, the pyrotechnic properties of other carbon-based substances, particularly carbon black were studied. The use of charcoal has been widely spread due to its unique chemical composition and superior combustion properties. However, due to the specific production process and the selection of materials for producing charcoal, it is difficult to achieve the same quality, i.e., chemical composition of charcoal. The use of other carbon-based substances may suppress those problems. Quaternary compositions containing charcoal or carbon black as a fuel and KNO_3, sulfur and phenol-formaldehyde resin were prepared and tested. Commercially available charcoal and carbon black were obtained for this initial research. The as-received materials, charcoal and carbon black, were characterized by SEM, EDS and particle size analyzer. SEM and EDS analysis were used to obtain information about morphology and semi-quantitative determination of the chemical composition and particle size analyzer for obtaining information about particle size and its distribution. The experimental values of heat of reaction and linear burning rate were compared. The average linear burning rate for pyrotechnic composition with carbon black of 7.33mm/s showed increase of 28.5% comparing to pyrotechnic composition with charcoal. Observed behavior suggests that this compound may be useful for a variety of pyrotechnic applications.*

Keywords: *energetic materials, linear burning rate, heat of reaction, carbon black, charcoal.*

1. INTRODUCTION

Pyrotechnic delays had been used since the first hand grenade has been made. They are used to provide a reproducible time interval between two energetic events. Until the mid-20th century black powder was materials of choice for delays [1,2]. Nowadays typically metals and other materials are used as fuels for delays since they have low production of gaseous products during the combustion and reproducible time intervals between two energetic events. Nevertheless, black powder can produce very reproducible intervals, but it must be vented due to the large amount of permanent gas generated during the combustion [3]. This disadvantage is prevented by adequate design of a fuze. Beside this, charcoal is both disadvantage and advantage of black powder. Charcoal is a natural solid fuel. It is produced by pyrolysis of wood. The physical and chemical properties are hard to define due to the nature of wood and technological parameters of carbonization. Beside those non reproducible parameters, charcoal still has superior properties like large surface area, approximately 1-3m^2/mg, heat conductivity and adsorption. It behaves like catalyst in combustion of black powder [4]. The chemical composition of charcoal is mainly carbon and in the small percentage there are also large number of different hydrocarbons, ash, moisture [5-6]. However, black powder is still in use nowadays and it has many modifications regarding its application.

The aim of this research was to overcome the disadvantage of non-reproducible parameters of charcoal. Knowing that charcoal consists mainly of carbon it came naturally to find substitute in a form of another carbon-based material. Nowadays, there are many carbon-based materials that have potential use in pyrotechnics. These are graphene, carbon nanotubes, carbon black etc. Carbon black is widely known for its use in different industries and as an additive in energetic materials, but it wasn't use in pyrotechnic compositions as a main fuel.

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The term carbon black refers to an industrial product which essentially consists of elemental carbon in the form of near spherical particles of colloidal size, coalesced into particle aggregates and agglomerates. It is produced by the partial combustion or thermal decomposition of hydrocarbons. The production process nowadays can be precisely controlled, and it that manner produced carbon black has a clearly defined properties [7].

Carbon black has a wide range of applications like fillers to improve mechanical, electrical and optical properties, in elastomers, plastics, paint, inks etc. The primary carbon black characteristics that influence the properties of carbon black compounds are the particle size, aggregate size, the morphology of the carbon black aggregates and their microstructure.

For the aim of this study, quaternary compositions containing charcoal or carbon black as a fuel and KNO_3, sulfur and phenol-formaldehyde resin were prepared and tested.

2. EXPERIMENT

2.1. Materials

The used KNO_3 powder, sulfur powder, willow tree charcoal, carbon black and phenolic resin were delivered by Trayal Corporation AD. Ethyl alcohol (96% v/v) was purchased from Sigma-Aldrich, USA. All used chemicals were analytical grade or higher and were used as received.

2.2. Preparation of charcoal and carbon black-based compositions

Pyrotechnic compositions were prepared by the following steps. First the fuels and oxidizer underwent a drying process in an oven for a duration of 3 hours at 60 ºC and 5wt.% of phenolic resin was dissolved in ethanol to obtain solution. Then, dry homogenization was performed in two phases. The first phase consisted of mixing the fuels, charcoal or carbon black and sulfur, until all components were evenly dispersed. Then KNO_3 was added, and all compounds were well mixed together. After that, phenolic resin solution was added into the dry oxidant-fuel composition and well mixed together in porcelain veneer. The as-prepared compositions were put in an oven for about 1 hour at 60 ºC to partially remove solvent. After 1-hour, semi-dried composition was mashed through 100 mesh sieve and returned to an oven for 3 hours at 60 ºC to remove remaining moisture content for further use in the following experiments.

Both pyrotechnic compositions have same weight ratios of KNO_3, sulfur, phenolic resin and depending on composition charcoal or carbon black, 75:5:5:15, respectively. Keeping the same ratio, it was possible to compare results depending on weather composition consisted of charcoal or carbon black as a main fuel.

2.3. Characterization of the raw materials

The surface morphology and semi-quantitative chemical element composition of charcoal and carbon black were employed by scanning electron microscope with Energy dispersive X-ray Spectroscopy (20 kV, JEOL 6610LV, Japan).

Particle size analysis of charcoal and carbon black was measured on Anton Paar PSA 1190 laser diffraction instrument in liquid mode. Water was used as carrier liquid, and Igepal CA-630 surfactant was used for improved wetting of particles. Particles were dispersed for 5 minutes with the use of stirring and 50 W power ultrasound. Particle size is determined according to Mie theory with values of refractive and absorption indexes of 2 and 1, respectively. The specific surface area (SSA) of samples was calculated with Anton Paar Kalliope software and represents the sum of the actual surfaces of each particle. For these calculations shape factor of 1 is used (which means that particles are like perfect spheres), and density determined on gas pycnometer Ultrapyc 5000 by Anton Paar.

2.4. Characterization of the pyrotechnic compositions

The heat of reaction measurements were conducted with isoperibolic calorimeter (IKA- Calorimeter C 2000 model). For this analysis samples were prepared in powder form, 3g in each polyethylene bag, with electric squib to initiate combustion. Three measurements of each composition are measured, and they were performed in an inert atmosphere of argon.

Linear burning rate was determined for both pyrotechnic compositions. Samples were measured and pressed into an aluminum alloy tube, with length 15mm, diameter 8mm and thickness of wall tube 2mm with 20 MPa of pressure on the hydraulic press. Five measurements of each composition were conducted to obtain more precise data. The data were collected by VOD 811 system with specially adjusted software for the correct display of lower combustion velocities.

. RESULTS AND DISCUSSION

3.1. Preparation of pyrotechnic compositions

Preparation of selected pyrotechnic compositions was conducted as described in section 2.2.

While preparing charcoal/KNO_3/S/phenolic resin composition there were no difficulties regarding technique used to prepare this composition. On the other hand, composition containing carbon black as a main fuel had shown problems in dry homogenization and mashing faze. Due to the high tendency of agglomeration of carbon black it was difficult to achieve homogeneous dry mixture of fuels and oxidizer. One of the possible solutions was to separate dry homogenization into a few smaller batches. Also,a major problem appeared after wet homogenization. During the mashing phase, it was hard to put through a sieve semi-dried mixture. The mixture was constantly “sticking” to a sieve. To untangle the problem, a limited amount of composition was put on a sieve and after all composition passed through the sieve, the sieve was cleaned with a brush to prevent sticking of next amount of semi-dried mixture.

3.2. SEM and EDS results

In Figure 1 and 2 SEM images with corresponding EDX spectra for charcoal and carbon black are shown, respectively.

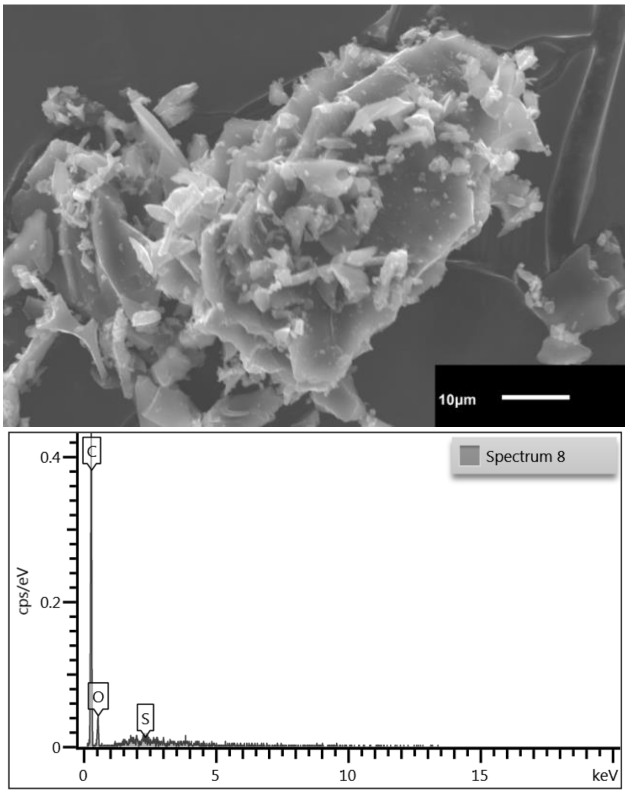
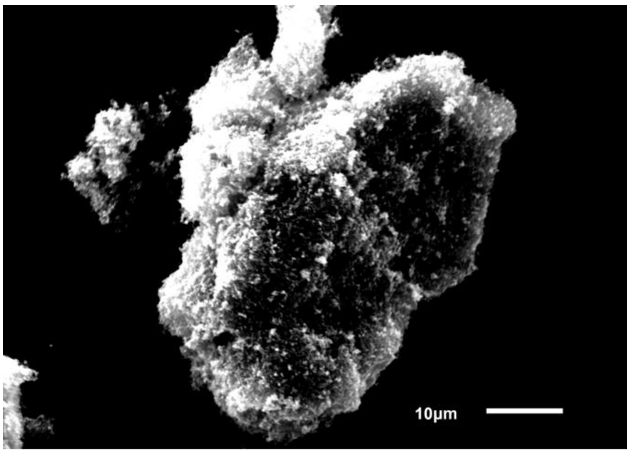


Figure 1. SEM image with corresponding EDS for charcoal



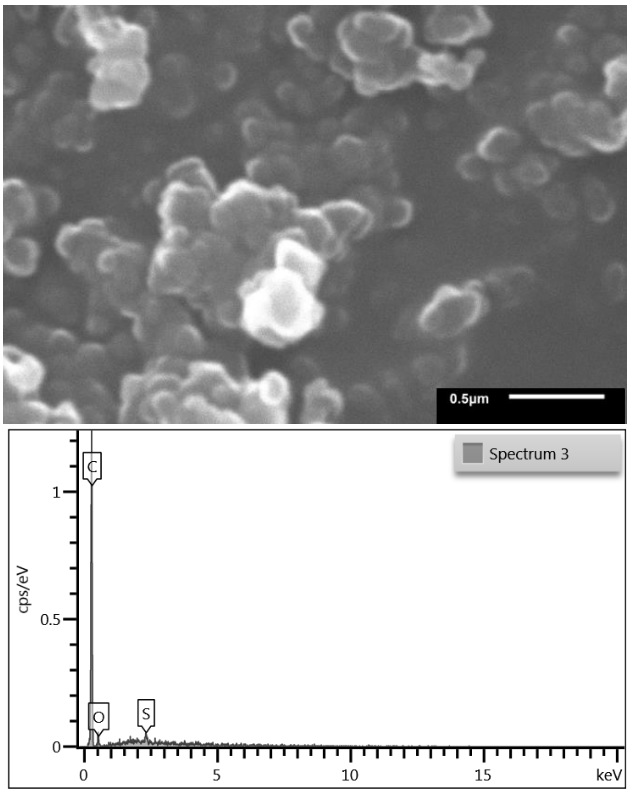


Figure 2. SEM images with corresponding EDS for carbon black

Figure 1 shows SEM image of charcoal where sample consist of broken pieces in different sizes and shapes. In Figure 2, are shown images of carbon black. First image, Figure 2, was captured with magnification of 1500, and it can be seen agglomerated sample of carbon black bigger than 10 μm compared to measurement bar of 10 μm on the image. On the image below, it’s presented sample of carbon black magnified 45 000 time, and captured particles are much smaller, and they are more likely to be found in carbon black composition than large agglomerate.

Table 1 shows the results from the surface element analyses of the two samples determined by SEM-EDS.

Table 1. SEM-EDS analysis results of charcoal and carbon black

Element	Charcoal (wt%)	Carbon black (wt%)
C	79.80	95.83
O	19.94	3.21
S	0.26	0.96
Total	100	100

The analyzed EDX spectra, Table 1, shows that charcoal and carbon black consist mainly of carbon. The charcoal’s degree of carbonization yields 79.80 wt% of element carbon and almost 20 wt% of other elements which are probably in the form of hydrocarbons, ash and moisture. Carbon black yields 95.83 wt% of carbon and in traces other elements like oxygen and sulfur.

3.3. Particle size analysis and specific surface area results

In Table 2 average volume weighted distribution results of five consecutive measurements and standard deviations are shown. Small standard deviations, which are in the range of less than one to a couple of percent compared to average values, indicate good dispersion of particles in carrier liquid and valid measurement results.

Table 2. Results of particle size and SSA analysis

Sample	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	D[4,3] (μm)	Span	SSA (m^2/g)
Charcoal	4.96 ±0.02	18.66 ±0.10	52.50 ±0.51	25.48 ±0.18	2.55 ±0.02	0.45 ±0.01
Carbon black	0.48 ±0.03	1.74 ±0.07	8.58 ±0.41	3.54 ±0.13	4.65 ±0.30	3.29 ±0.15

In Figures 3 and 4 differential and cumulative particle size distributions are shown.

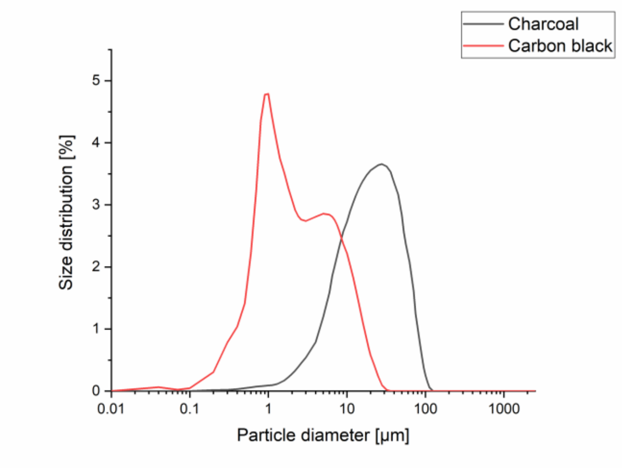


Figure 3. Differential particle size distribution of charcoal and carbon black

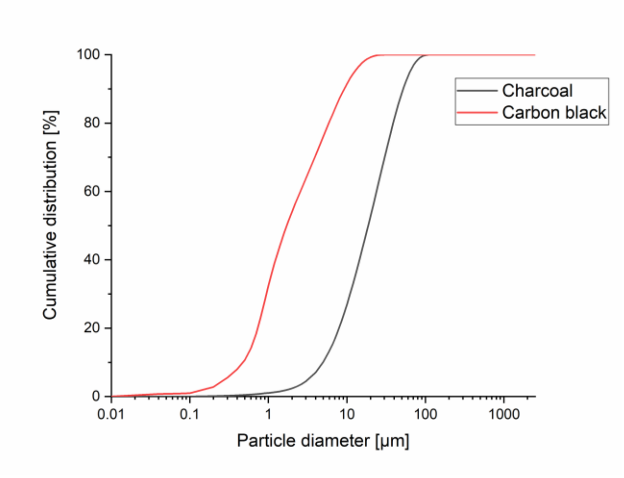


Figure 4. Cumulative particle size distribution of charcoal and carbon black

It is obvious that carbon black consists of much smaller particles than charcoal. Mean particle size of carbon black is more than 7 times smaller than of charcoal. Carbon black has a significant portion of particles smaller than 1 μm (approximately 30% volume weighted), while charcoal has only 1% of particles smaller than 1 μm. The maximum particles size of carbon black is 20 μm, and of charcoal is 100 μm. This leads to a much higher specific surface area of carbon black (3.29 m^2/g) compared to charcoal (0.45 m^2/g), which is favorable parameter for fast burning pyrotechnic compositions. Also, width of particle size distribution is much wider for carbon black compared to charcoal, span is 4.65 versus 2.55. It can be seen from Figure 3 that particle size distribution of carbon black is bimodal, with main maximum distribution of particles around 1 μm and 5 μm, while particle size distribution of charcoal is monomodal, with main maximum distribution of particles around 30 μm. Materials which have polydisperse particles usually can be pressed to a higher level due to more filled voids, and in that way higher densities can be achieved, which leads to more energy confined in the same volume.

3.4. Heat of reaction results

The heat of reaction values are presented in Table 3. Average values for charcoal-based and carbon black-based composition are 2774.0 J/g and 2650.2 J/g respectively. Standard deviation for charcoal-based and carbon black-based composition are 15.99 J/g, and 25.12 J/g, respectively. Standard deviation indicates that measurements were performed correctly. Slightly higher standard deviation for carbon black compositions of 25.12 J/g may be due to the difficulties regarding preparation technique described in section 3.1 that had brought to the less homogeneous mixture and may lead to the incomplete combustion as carbon black tends to agglomerate in composition.

Average value for charcoal-based composition is 123.83 J/g higher form average value for carbon black-based composition. Knowing from EDS analysis that charcoal contains O in 19.94 wt% and carbon black only 3.21 wt% of O shows that oxygen balance is higher for charcoal-based compositions. This indicates higher calorific value for charcoal-based compositions.

Table 3. Heat of reaction results for charcoal and carbon black-based compositions

Sample	Heat of reaction [J/g]	
	Charcoal based PC	Carbon black-based PC
1	2761.7	2648.4
2	2792.1	2626.5
3	2768.3	2676.6
Average value	2774.0	2650.2
Standard dev.	15.99	25.12

3.5. Linear burning rate results

The linear burning rate values are shown in Table 4. Standard deviation for linear burning rate for charcoal-based compositions is 0.26 mm/s and for carbon black compositions is 0.24 mm/s which indicates that measurements were performed correctly. It is obvious that carbon black composition has a higher value in linear burning rate than charcoal-based composition. Average values for charcoal-based and carbon black-based compositions are 5.7 mm/s and 7.33 mm/s, respectively. There is an increase of 28.5% in linear burning velocity in favor of carbon black composition. Higher SSA, smaller mean particle size of carbon black and more energy confided in same volume resulted in faster burning of pyrotechnic composition with carbon black.

Table 4. Linear burning rate results for charcoal and carbon black-based compositions

Sample	Linear burning rate [mm/s]	
	Charcoal based PC	Carbon black-based PC
1	5.8	7.0
2	5.6	7.5
3	5.6	7.3
4	5.4	7.6
5	6.1	7.3
Average value	5.7	7.3
Standard dev.	0.26	0.24

4. CONCLUSIONS

Charcoal and carbon black-based delay pyrotechnic compositions were prepared and examined to research the possibility to incorporate other carbon-based materials instead of charcoal in pyrotechnic delay. Preparation technique showed difficulties regarding preparation of carbon black-based compositions due to the tendency of carbon black to agglomerate. EDS analysis of charcoal and carbon black offered different views on elemental semi-quantitative chemical composition. Charcoal has higher wt% of oxygen 19.94, probably in the form of moisture, hydrocarbons, ash etc., which directly increase an oxygen balance for charcoal-based composition. Also, charcoal-based composition showed higher values for heat of reaction of 2774.03 J/g compared to carbon black-based composition of 2650.2 J/g. Mean particle size of carbon black is more than 7 times smaller than of charcoal and it has approximately 30% of volume weighted of particles are smaller than 1 μm. This implies higher SSA of carbon black and increase in average linear burning rate of 28.5% for carbon black-based composition compared to charcoal-based composition. Those attributes suggest that particle size and its distribution are probably the most important physical properties of carbon black in terms of end-use applications. For some future study, this work provides an insight into difficulties regarding preparation of carbon black-based composition and a possible new idea for preparation of that composition in some different techniques.

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References

[1] CONKLING, J. A.; MOCELLA, C. J: *Chemistry of Pyrotechnics: Basic Principles and Theory*, 2nd ed.; CRC Press, Taylor & Francis Group: Boca Raton, 2011.

[2] WILSON, M. A.; HANCOX, R. J.: *Pyrotechnic Delays and Thermal Sources" in Pyrotechnic Chemistry: Pyrotechnic Reference Series No. 4*, Kosanke, K.; Kosanke, B.; Journal of Pyrotechnics, Inc: Whitewater, CO, 2004.

[3] Poret J.C. et al.: *Environmentally Benign Pyrotechnic Delays*, 38th International Pyrotechnics Seminar, Denver, Colorado, 10-15 June 2012, p. 494-500.

[4] [4] J.H. MC LAIN: *Pyrotechnic from the viewpoint of Solid-State Chemistry*, Franklin Institute Press, USA, 1980.

[5] I. GLASSMAN: *Combustion*, 3rd Edition, 1996.

[6] MOJSILOVIC J. et al.: *Design of suitable pyrotechnic delay composition with widely used components*, 10th International scientific conference on defensive technologies OTEH 2022, Belgrade, Serbia, 13.-14. October 2022. p.150 -154.

[7] DONNET, J. B.: Carbon Black: Science and Technology, 2nd edition Revised and Expanded Marcel Dekker, inc., USA, 1993.