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Research on Gas Producing Time Delay Pyrotechnic Compositions Based on Black Powder and Phenol-Formaldehyde Resin

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In the past few years, we have witnessed that due to the pandemic and wars, some countries have limited their export of various ingredients. The request has been made to create a time delay pyrotechnic composition with easily accessible ingredients. For that purpose, black powder with addition of phenol formaldehyde resin was a possible solution. This study aims to show an optimization of the ratio in the fuel-oxidant mixture and how this ratio influences the properties of pyrotechnic compositions. The stoichiometric ratios were determined by using the oxygen balance (OB) and pyro valence (PV) values. The linear burning rate was measured using a VOD 811 measuring system for some typical compositions which were pressed into aluminium tubes. The calorimetric bomb was used in the experiments with an inert gas supply to determinate the heat of reaction and the closed-vessel test was used to measure the production of gaseous products. The theoretical maximum density was calculated using ingredients' density measured with gas pycnometer ULTRAPYC 5000 with an inert gas supply nitrogen or helium. After these tests, it was concluded that pyrotechnic composition with more than 25 wt.% of charcoal does not satisfy requirements for a gas producing pyrotechnic composition. The minimal requirements can be satisfied with pyrotechnic compositions that consist of 75-80 wt.% of potassium nitrate, 5-15 wt.% of charcoal, 5-10 wt.% of sulphur and remaining 5 wt.% comprising of phenol-formaldehyde resin.

Key words: **time delay pyrotechnic composition, charcoal, theoretical maximum density, heat of reaction, linear burning rate, gas producing composition.**

Introduction

AMONG the variety of energy-intensive compositions, delay pyrotechnic compositions serve to create time delays of the required duration. The need to ensure a time delay in the operation of pyrotechnic products arose with the appearance of black powder and the first fuzes, bombs, hand grenades and rockets. The delay is necessary for an explosive ordnance to move to a safe distance, and to detonate the charge at the right moment [1]. Pyrotechnic delay compositions can be considered gasless or gas-producing depending on the quantity of gas generated during the combustion. Typically, gasless delays are used in sophisticated projectiles and gas-producing delays are used for inexpensive munitions such as hand grenades and signal devices. In the earlier research it has been found that, if approximately 50% of the reaction products are gaseous, it can be considered that time delay composition is gas producing [2]. The advantages of gas producing delay compositions over gasless systems are in their ability to provide accurate delay time, long-term storage stability, and available ingredients. The disadvantage of the system lies in the effect of external pressure on their burning rate which can be overcome by providing an adequate fuze design [3]. Gas producing time delay pyrotechnical compositions made of black powder with an addition of phenol formaldehyde resin were considered in this paper. Observed pyrotechnic compositions consist of 65-80 wt.% of potassium nitrate, 5-25 wt.% of charcoal, 5-10 wt.% of sulphur with rest comprising of phenol-formaldehyde resin. Some of the important characteristics of these delay compositions are gaseous combustion products, constant burning rate, economically and easily accessible ingredients and long-term storage stability. The object of this study is to predict a trend of different oxidant to fuel ratios of pyrotechnic compositions. The methods used to explain these mechanisms were theoretical calculations of oxygen balance and pyro valence values and determinations of heat of reaction, theoretical maximum density, gas producing characteristic and linear burning rate values.

Experiments

Ingredients and Preparation

All ingredients, except of charcoal, have small variations in quality. There are two main factors which affect charcoal's quality the most: type of materials and the manufacturing process. There are abundant sources of natural materials that can be potentially used to create an endless variety of charcoals. But, typically, softer types of wood, such as

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willow, alder and poplar have been used mostly. [4] Charcoal is a natural solid fuel, which is produced by pyrolysis or carbonization of wood. The precise chemical composition and physical appearance are difficult to define. It depends on the degree of carbonization, temperature and pressure of the process. This natural material contains carbon, moisture, ash-generating minerals, and a large number of different hydrocarbons that volatilize when combustion is initiated [4, 5]. It has a large surface area, approximately 1-3m^2/mg, heat conductivity and adsorption [5,6]. Thus, black powder has a high burning rate and charcoal is used as a catalyst. Chemical compositions of charcoal from literature [2], [7-10] and thermodynamic code EXPLO5 are presented in Table 1. This implies that charcoal contains largely of carbon, and carbon as an approximation in calculations was used for easier determination of OB and PV in this paper . The charcoal used in this paper has a willow tree (Salix) origin.

Table 1. Charcoal formulations from different sources

Number	Charcoal formula	Source
1	C_6H_{2O}	Šidlovski [7]
2	$C_{16}H_{10}O_2$	Maksimović[8], Cok-ling[2]
3	$C_{20}H_7O$	Orbović [9]
4	$C_{42}H_{60}O_{28}$	Koch [10]
5	$C_{7,2}H_{4,99}O_{0,52}$	EXPLO5
6	$C_{10}H_{4,77}N_{0,04}O_{1,23}Ca_{0,003}$	EXPLO5

Mixing process

The following substances were used to prepare formulations (Table 2) and perform the experimental study: potassium nitrate as an oxidizer, charcoal and sulphur as fuels, and phenol-formaldehyde resin as a binder.

Table 2. Selected formulations with wt. % of ingredients

	TD-1	TD-3	TD-4	TD-6	TD-7
KNO3	65	75	80	75	75
C	25	15	10	5	10
S	5	5	5	15	10
C13H12O2	5	5	5	5	5

The method of preparation consists of the following operations:

- weighting of ingredients;
- drying of oxidizer and fuels in an oven at 60°C for 3h;
- dissolving the phenol-formaldehyde resin in a solvent;
- two phases of dry homogenization. The first phase was performed by mixing fuels until all components were evenly dispersed, then in the second phase an oxidizer was added and all compounds were well-mixed together;
- wet homogenization was performed with well mixed ingredients from dry homogenization with the addition of dissolved binder;
- mashing phase consists of manual sieving of the wet mixture through a sieve;
- drying in an oven at 60°C for 4h to remove remaining moisture content;
- the last operation was packing into hermetic containers [10].
- All ingredients were delivered by Trayal Corporation AD (commercial quality) and formulations TD-1, TD-3, TD-4, TD-6 and TD-7 from Table 2 were selected to determinate linear burning rate, the heat of reaction and predict the burning behavior of formulations by the closed-vessel system [12].

Methods

Oxygen balance and pyro valence

The oxygen balance and pyro valence values were calculated for seven compositions from Table 3. It was assumed that during the combustion each reactant would chemically react to form a product in the most stable oxidation state.

Heat of reaction

The heat of reaction was determined by isochoric combustion in a calorimetric bomb, using the IKA-Calorimeter C 2000 model. The experiments were performed in the absence of oxygen with an inert gas supply to determinate the heat of reaction value. A mechanical mixture of 3 g was used in powder form to determinate the value of heat released during the reaction. For each pyrotechnic composition, three measurements were performed.

Theoretical maximum density

Each ingredients' density was measured with gas pycnometer Ultrapyc 5000 by Anton Paar (Fig.1).

Figure 1. Ultrapyc 5000 by Anton Paar

The experiments were performed with an inert gas supply of nitrogen or helium. Each ingredient was placed in a sample cell in a powder form. Potassium nitrate, sulphur and phenol-formaldehyde resin were measured in nitrogen atmosphere while charcoal, due to its high reactivity, was measured with helium. The theoretical maximum densities (TMD) of all seven compositions (Table 3) were calculated using the mass fraction and density of each ingredient in the mixture.

Table 3. Selected formulations of time delay pyrotechnic compositions

	TD-1	**TD-2**	**TD-3**	**TD-4**	**TD-5**	**TD-6**	**TD-7**
KNO_3	65	70	75	80	85	75	75
C	25	20	15	10	5	5	10
S	5	5	5	5	5	15	10
$C_{13}H_{12}O_2$	5	5	5	5	5	5	5

Linear Burning rate

Burning characteristics of any multicomponent solid fuels depend on many significant parameters such as overall composition, fuel and oxidizer particle size, adequate interparticle contacts between reactants, an adequate technique of mixing, bulk thermal conductivity and heat of reaction of the mixture, reaction rate progress, reaction zone temperature and pressure [12]. It is a self-propagating reaction in solid mixtures with a strongly exothermic reaction when a considerable amount of heat is evolved in the chemical charge. The linear burning rate can be determined based on the physicochemical property of the ingredients and their relative proportion. The purpose of this time delay composition is to be able to provide a specific time between two events and it also has a role to ignite the next mixture in the pyrotechnic train. Therefore, it is important to define the precise time and flux of gaseous products so they can fulfil their required function. For each composition, five tubes were tested. A specific amount of each pyrotechnic composition was measured and pressed into an aluminum alloy tube (height 15mm, radius 8mm and wall tube thickness 2mm) with 20 MPa of pressure on the “DUNKES” hydraulic press. The linear burning rate was determined with VOD 811 system with specially adjusted software for the correct display of lower combustion velocities.

Closed vessel system

The selection of an oxidizer, fuel and binder for pyrotechnic composition and their weight ratio determines the heat output as well as the gas output for the mixture under consideration [2]. For time delay compositions, considered in this paper, it is very important to have the first information on gas generating possibilities, especially on how many gas products are going to be produced in a function of time.

The pressure of combustion products is a very distinctive characteristic of every pyrotechnic composition and it is strongly influenced by the nature of ingredient’s oxygen/fuel ratio [11]. In this study the pressure of combustion products was measured in a closed vessel. Every sample prepared for the experiment consisted of 3g of pyrotechnic composition in powder form placed in polyethylene containers and fitted with an electric igniter. The polyethylene containers were then placed in a bomb and an electric igniter was connected onto the connectors on the bomb cover. The Tektronix DPO 4054 Digital Phosphor Oscilloscope (500MHz-2ns) was used to measure data.

Results and Discussion

Oxygen balance and pyro valence

Seven compositions were selected to determinate OB and PV and they are presented in Table 4. The $\Omega(CO_2)$ of all compositions lies in the range of -63.08% to +34.3%. Pyro valence was calculated for all compositions and it is noticeable that PV approach has a similar trend when it comes to assuming the products of reaction as OB method.

Table 4. Selected formulations of pyrotechnic compositions with OB and PV values

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7
KNO_3	65	70	75	80	85	75	75
C	25	20	15	10	5	5	10
S	5	5	5	5	5	15	10
$C_{13}H_{12}O_2$	5	5	5	5	5	5	5
$\Omega(CO_2)$ [%]	-63.08	-52.6	-37.3	-12.55	+34.3	-9	-25.8
PV	+7.22	+5.05	+3.4	+1.47	-0.42	+1.36	+2.32

Heat of reaction

For each pyrotechnic composition, three measurements were performed and an average value was presented in Fig.2. The heat output data shows that values lies in a range of 2114.9 J/g up to 3054.8 J/g. The highest heat of reaction value is with the composition TD-4 (3054.8 J/g). It contains the highest content of oxidizer (80 wt.%) and OB is -12.55%. It is interesting to note that composition TD-6 has the second highest value of energetic potential of 3020.5 J/g, the highest content of sulphur and highest OB (-9%) of all compositions. This result can be explained by the dual nature of sulphur. Depending on the conditions, sulphur can behave as an oxidizer or as a fuel in the combustion process [12]. The poorest value belongs to TD-1 composition, (2114.9 J/g), so it can be concluded that the highest wt. percentage of charcoal definitely has a negative effect on the heat output.

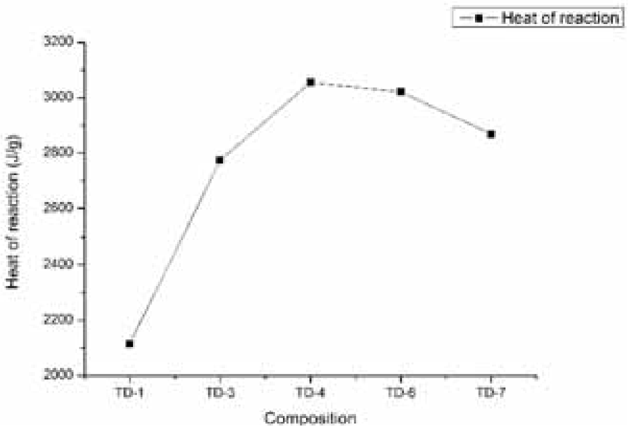

Figure 2. Selected compositions and their heat of reactions values

Calculation of theoretical maximum density

The theoretical maximum densities (TMD) of all seven compositions were calculated using the mass fraction and density of each ingredient in the mixture. The results of all seven pyrotechnic compositions and their TMD are presented in Fig.3. It is observed that, starting from pyrotechnic composition TD-1 (1,96 g/cm^3), there is an increase of TMD values, almost linear line until TD-5 composition (2,05 g/cm^3). Although there is a decreasing trend in TD-6 (2,04 g/cm^3) and TD-7 (2,02 g/cm^3), there is a relatively small standard deviation with TD-4, TD-5, TD-6 and TD-7 of 0.013%. The theoretical maximum density represents an important parameter of every energetic material. TMD shows the maximum amount of energy that can be stored into the system.

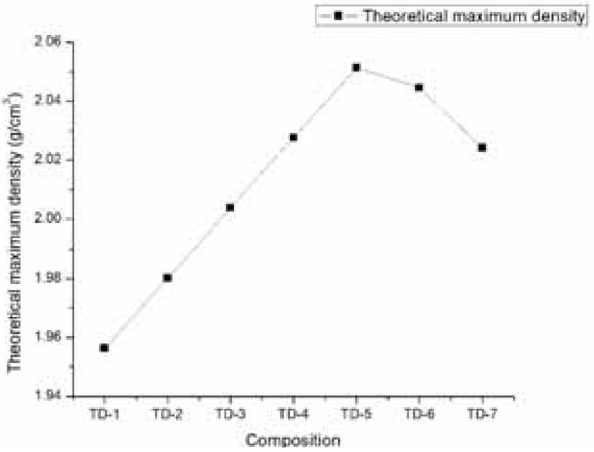

Figure 3. Pyrotechnic compositions and their theoretical maximum density

Comparative analysis of theoretical maximum density, oxygen balance and heat of reaction

Observing the heat of reaction, TMD and OB values for selected compositions (Fig.4), it can be concluded that there are similar trends and that there is some kind of correlation between the parameters. The highest values of TMD, OB and heat of reaction belong to TD-4, TD-6 and TD-7 compositions. For example, pyrotechnic composition TD-6 with Ω (CO2) closes to equilibrium of -9% has the highest TDM and the second highest heat of reaction value and pyrotechnic composition TD-1 with Ω (CO2) of -63.08% has the smallest TMD and heat of reaction value. If we look at TMD as the maximum amount of energy stored into the system, then we can conclude that depending on the conditions such as initiation, form in which pyrotechnic compositions is used, compressed or loosed, type of delay tube and etc., TMD represents a good start for choosing pyrotechnic composition.

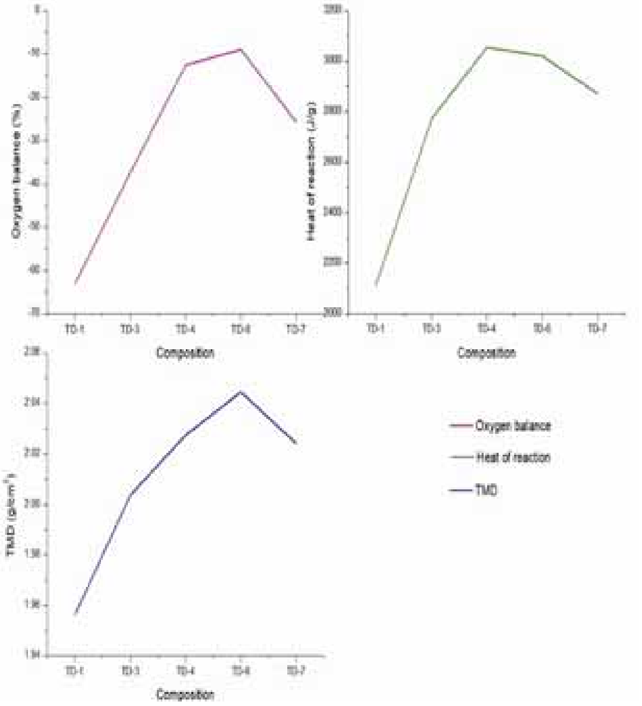

Figure 4. Comparison of graphics of theoretical maximum density, oxygen balance and heat of reaction

Determination of gas producing characteristic

The gas-producing characteristics were measured in a manometric bomb. For each composition three measurements were taken and the average value was calculated. The results are shown in Fig.5.

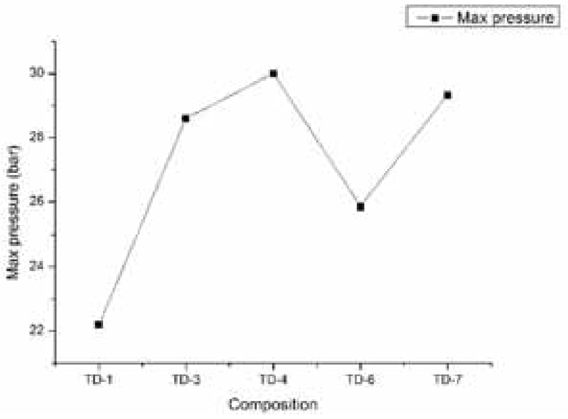

Figure 5. Selected compositions and their maximum pressure

Results in Fig.5 and Table 5 show that compositions TD-3, TD-4, TD-6 and TD-7 have relatively small scattering values in both maximum pressure of combustion products (P_{max}) and time to reach P_{max} (t_{max}), so they have similar behavior when it comes to gas-producing characteristics.

Table 5. Measured time (t_{max}) to reach maximum pressure (P_{max}) for selected compositions

Composition	**TD-1**	**TD-3**	**TD-4**	**TD-6**	**TD-7**
P_{max} [bar]	22.2	28.6	30	25.87	29.33
t_{max} [ms]	121.73	47.27	39.87	51.53	36.2

Pyrotechnic composition TD-1 has a huge drop compared to the four mentioned in both maximum pressure of combustion products (P_{max}) and time to reach P_{max} (lowest t_{max}). This is attributed to the presence of a high mass percentage of charcoal which implies that due to its nature, charcoal has an affinity to "suffocate" combustion process. Furthermore, this implies that incomplete combustion has occurred with TD-1 composition [12].

Linear burning rate

Data from the linear burning test are shown in Fig.6. For each composition, five tubes were tested, and an average value was calculated. Results in Fig.5 reveal that the fastest burning belongs to composition TD-1 and, from that point, there is a decreasing trend of burning time which follows until composition TD-6. It is interesting to note that the pyrotechnic composition TD-1 has the highest OB value, the lowest value of heat of reaction and poorest, substandard values of gas-producing characteristics; this implies that burning characteristics depend on properties like inter-particle contacts between reactants, heat conductivity increases if the pyrotechnic composition is in a compressed form.

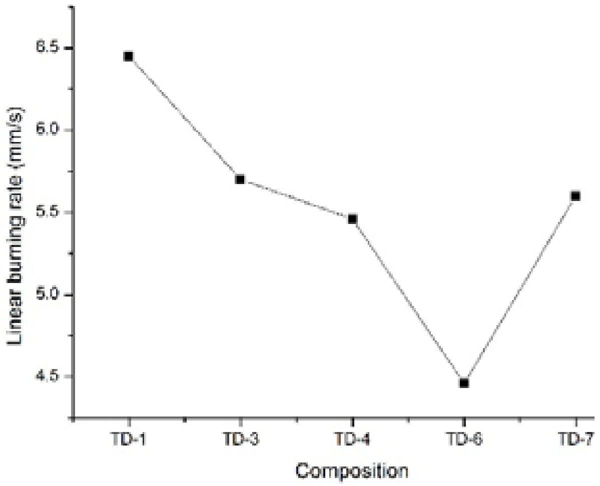

Figure 6. Average linear burning rate for selected pyrotechnic composition

Conclusion

The main focus of this work was to incorporate easily acceptable ingredients to produce desired time delay effect. In this work, black powder compositions with addition of phenol-formaldehyde resin were analyzed and compared. Any change in the ratio of the pyrotechnic composition essentially affects the equilibrium. For gaseous, time delay pyrotechnic composition is important to have a well-balanced combination of gaseous and condensed products of combustion. It was important to suppress explosive power of black powder. It was managed with addition of phenol-formaldehyde resin.

The obtained data shows that combustion of pyrotechnic compositions is a complex thermodynamic process and that it changes with a slight change in oxidant-fuel ratio. Therefore, the primary functions of gaseous time delay compositions are satisfied with compositions TD-3, TD-4, TD-6 and TD-7. Those pyrotechnic compositions can be used in different types of ammunition depending on the required effect. The composition TD-1 does not satisfy the minimum of performed tests. However, for a more precise determination of time delay compositions, more tests must be performed for full characterization. For some future work, it would be interesting to perform an analysis with active carbon and carbon black instead of charcoal or with different type of charcoal.

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Crni barut u ulozi gasnih usporačkih pirotehničkih sastava

U poslednjih nekoliko godina svedoci smo globalne pandemije i ratova koji za posledicu imaju da pojedine zemlje uskraćuju izvoz odredjenih sirovina. Pojavila se potreba da se od sirovina iz široke upotrebe napravi gasovita usporačka smeša. U tu svrhu dizajnirana je uposoračka pirotehnička smeša koja je napravljana od crnog baruta sa dodtakom fenol formaldehidne smole. Ovaj rad teži da prikaže kako se optimizacijom goriva i oksidansa može uticati na sagorevanje pirotehničkih sastava. Teoretski su izračunate vrednosti bilansa kiseonika i piro valence. Za određene pirotehničke sastave merena je linearna brzina sagorevanja sa VOD 811 sistemom. Energetski potencijal je izmeren u kalorimetrijskoj bombi u atmosferi argona. Maksimalni pritisak produkata sagorevanja kao i vreme kašnjenja su određeni u manometarskoj bombi. Gustina ulaznih sirovina je izračunata pomoću gasnog piknometra ULTRAPYC 5000 u atmosferi azota ili helijuma. Nakon izvršenih opita došlo se do zaključka da usporački sastav sa više od 24 mas.% drvenog uglja ne zadovoljava zahteve za gasne usporačke sastave. Minimalne zahteve su zadovoljili sastavi sa 75-80 mas.% kalijum nitrata, 5-15 mas.% drvenog uglja, 5-10 mas.% sumpora i 5 mas.% fenol formaldehidne smore kao vezivne komponente.

Ključne reči: **usporačke pirotehničke smeše, drveni ugalj, teorijski maksimalna gustina, energetski potencijal, linearna brzina sagorevanja.**