

## Article

# Study on Detonation Characteristics of Ammonium Nitrate-Polyhydroxy Alcohol Mixtures

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**Abstract:** This paper presents the results of detonation parameters for ammonium nitrate-polyhydroxy alcohol mixtures and ternary explosive compositions modified by flaked aluminium. The detonation velocities, overpressures of blast waves and their specific impulses were determined. It was shown that the viscosity of liquid fuels is the leading property that determines the detonation parameters of the tested compositions.

**Keywords:** ANFO; alcohol addition; detonation velocity; modified ANFO



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## 1. Introduction

Explosives based on ammonium nitrate can be defined as mixtures of an oxidiser—pure ammonium nitrate (AN) or partially replaced by other nitrates—with flammable substances. The main reason for the fuel addition in mixtures with AN is to reach a specific oxygen balance, which indicates an increase in thermodynamic parameters and detonation parameters. Fuel also has an influence on detonability increase—decreasing of critical diameter and initial mass. Ammonium nitrate explosives are based on black powder, so, not surprisingly, the first known explosive containing AN was ammoniakkrut. This composition, patented in 1867 by Swedish chemists J. H. Norrbin and J. Ohlsson, was a mixture of ammonium nitrate (80%) and charcoal (20%) [1].

From the chemical point of view, fuels used in ammonium nitrate explosives can be divided into organic and inorganic substances. Examples of organic fuels are chemical compounds: urea, pentaerythritol, sorbitol and mannitol [2–5]; groceries: flour, sucrose, milk powder [6], powdered substances of natural origin: corncob, rice straw, sugarcane bagasse [7] or hay [8]; materials obtained from recycled tires [7,8]; or activated carbon [9] or biochar [10].

The most commonly used materials counted as inorganic substances are metal powders, especially aluminium powders with varying degrees of fineness. The first explosives called ammonals, which contained ammonium nitrate, aluminium powder and charcoal, were patented in 1900 by G. Roth and were produced by his company in Felixdorf (Austria) [1]. However, the real development of aluminised explosives took place after World War I, when aluminium prices dropped. The majority of the studies were oriented towards the influence of the structure and the fineness of different substances on detonation parameters [11–14].

While the previously mentioned fuels are in a solid-state, in the case of ANFO explosives, liquids, mostly mineral oils, are used. Although ANFO explosives have been known and used for many years, their various parameters are being examined even today [14–21].

These studies concern the structure and morphology of nitrate granules and their mixtures with different oil types [17–19]. Many studies have also been published on aluminium powder influence on detonation parameters of ANFO explosives [14,21]. One of the original suggestions [20] is to replace fuel oils in ANFO with alcohols: methanol, ethanol, propane-2-ol, propane-1,2-diol, ethylene glycol or glycerol. The authors of [20] present the results of their research on ammonium nitrate mixtures with the above-mentioned alcohols, in which they utilised infrared spectroscopy, X-ray diffraction and scanning electron microscopy. However, they did not measure any detonation characteristics, which is the primary goal of this paper.

## 2. Experimental Section

### 2.1. The Characteristics of Applied Raw Materials and the Methodology of Sample Preparation

For this research, porous ammonium nitrate distributed by Yara Poland Sp. z o. o. was chosen. The bulk density of this ammonium nitrate was  $0.8 \text{ g/cm}^3$ . Based on the analysis of physical properties, the following polyhydroxy alcohols were chosen as potential fuels: ethan-1,2-diol (ED), propan-1,3-diol (PD), propan-1,2,3-triol (PT) and butan-1,4-diol (BD). Moreover, two monohydroxyl alcohols (ethanol (ET) and propane-2-ol (PO)) and fuel oil were used for comparison. Table 1 presents the selected properties of the fuels used in this research.

**Table 1.** Properties of fuels used in research.

Oxygen Fuel	Oxygen Balance [%]	Dynamic Viscosity [mPa·s] in 25 °C *	Flashpoint [°C] *
Ethanol	−208.70	1.074	17
Ethan-1,2-diol	−129.03	16.01	111
Propan-2-ol	−240.00	2.038	12
Propan-1,3-diol	−168.42	43.4	345
Propan-1,2,3-triol	−121.74	954	177
Butan-1,4-diol	−195.56	84.9 (20 °C)	121
Fuel oil	−348.24	150	>55 (closed-cup)

\* <https://pubchem.ncbi.nlm.nih.gov> (accessed on 20 August 2022).

Due to the differences in oxygen balance (OB) values, calculations were performed aimed at the determination of the fuels content in AN explosives with zero oxygen balance. The results of these calculations are presented in Table 2.

**Table 2.** Fuel content in explosives with AN with zero oxygen balance.

Organic Fuel	Content [%]
Ethanol	8.75
Ethan-1,2-diol	13.42
Propan-2-ol	7.69
Propan-1,3-diol	10.61
Propan-1,2,3-triol	14.11
Butan-1,4-diol	9.28
Fuel oil	5.80

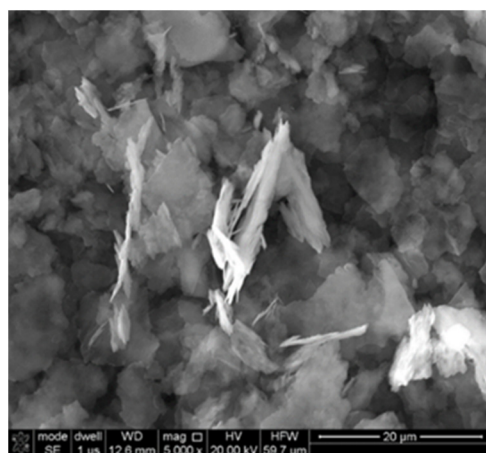
In some cases, the amount of alcohol needed to obtain a composition with zero oxygen balance is high, e.g., propane-1,2,3-triol or Ethan-1,2-diol. An attempt was made to check the possibility of obtaining a zero-oxygen balance mixture for AN and ED in the 87:13

ratio (by mass). Ammonium nitrate did not absorb alcohol completely, resulting in over-moisturising of AN granules. These granules agglomerated easily and the mixture was not homogeneous enough. Due to this, compositions analogous to classical ANFO explosives, in which the oxidiser constitutes 94% of the mass, were chosen. Oxygen balances of prepared compositions are presented in Table 3.

**Table 3.** Oxygen balance of ammonium nitrate mixtures with organic fuels 94/6 (by mass).

Explosive	Organic Fuel	Oxygen Balance [%]
ANFO	Fuel oil	−2.09
ANPT	Propan-1,2,3-triol	11.49
ANPD	Propan-1,3-diol	8.69
ANPO	Propan-2-ol	4.40
ANE	Ethanol	6.28
ANBD	Butan-1,4-diol	7.07
ANED	Ethan-1,2-diol	11.06

Due to the lower fuel content, compositions based on alcohol had a positive oxygen balance. Mixtures with flaked aluminium addition were tested in order to take advantage of the oxygen excess. The aluminium, BLITZ ALUMINIUM DEPUVAL 3083 ( $Al_f$ ) produced by Benda-Lutz, has an average particle size of 12  $\mu\text{m}$ , residue on sieve 45  $\mu\text{m}$  max. 0.8% and bulk density of 0.4  $\text{g}/\text{cm}^3$  (Figure 1). Oxygen balances of aluminised compositions are presented in Table 4.



**Figure 1.** SEM photo of  $Al_f$  powder.

**Table 4.** Oxygen balances of aluminised compositions.

Explosive Composition	Organic Fuel	Aluminium Content [%]	Oxygen Balance [%]
ANFO10	Fuel oil	10	−10.77
ANED5	Ethan-1,2-diol	5	6.06
ANED10	Ethan-1,2-diol	10	1.06
ANED15	Ethan-1,2-diol	15	−3.93

## 2.2. Research Methodology

### 2.2.1. Detonation Velocity Measurement

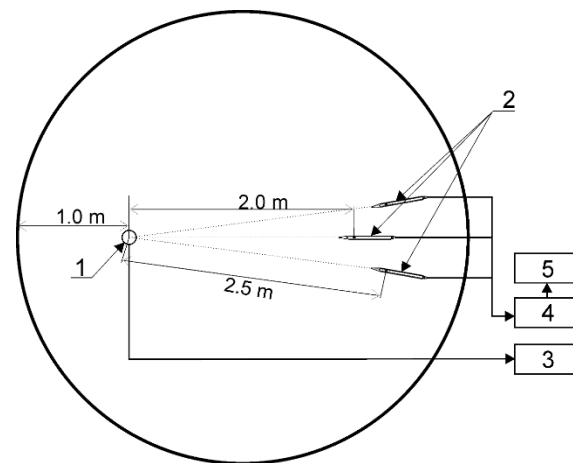
Detonation velocity measurements were made using the short-circuit method. The shells of tested explosives were made of PVC pipe with an inner diameter of 46 mm and a

wall thickness of 1.8 mm. Four short-circuit sensors were placed in the shells at a distance of 40 mm between subsequent sensors and 15 mm from the last sensor to the bottom of the charge.

### 2.2.2. Measurement of Air Blast Wave's Overpressure

Measurements of the blast wave's overpressure were carried out by means of piezoelectric sensors from PCB Piezotronics. The measuring system consisted of four 137A series sensors connected to an oscilloscope with the signal conditioner. The sensors were placed so that the distance between the load and the sensors' pair was 2 m and 2.5 m.

The charges of 300 g were prepared by mixing the ingredients until the AN completely absorbed the fuel. Materials were made immediately before testing to avoid water absorption from the air and the outflow of liquid fuel from the AN granules. The loads were hung in the bunker at the sensors' height and over 1 m from the nearest bunker wall. Two to three tests were performed for each type of explosive, with synchronous measurement of overpressure and detonation velocity. Figure 2 shows the diagram of the system for the air blast wave overpressure measurement.



**Figure 2.** Diagram of system for air blast wave overpressure measurement. 1—explosive charge, 2—pencil probes, 3—time meter, 4—signal conditioner, 5—oscilloscope.

The measurement results obtained using this method are affected by disturbances that may originate from the measuring system's electrical disturbances, electrical network or mechanical disturbances originating from vibrations of the mounting system of pressure sensors. In order to normalise blast wave pressure histories and minimise disturbances on the measured characteristics of the blast wave, the obtained overpressure histories were approximated with a modified Friedlander Equation (1):

$$P = P_S e^{-at} \left( 1 - \frac{t}{t^+} \right) \quad (1)$$

where  $P_S$  is the peak overpressure immediately behind the primary shock,  $t$  is the time after the arrival of the primary shock at the gauge location and  $a$  and  $t^+$  are constants.

## 2.3. Research Results

### 2.3.1. Results of Detonation Velocity Measurements

At the first stage of experiments, research on the influence of ethan-1,2-diol content on the detonation velocity and indirectly on its mixtures' detonability with ammonium nitrate was carried out. ED is characterised by one of the most positive oxygen balances among the selected alcohols (Table 1). Table 5 presents the results of the above-mentioned measurements.

**Table 5.** Dependence of detonation velocity of tested mixtures on ethan-1, 2-diol (ED) alcohol content.

ED Alcohol Content [% by Mass]	Density [g/cm <sup>3</sup> ]	Detonation Velocity [m/s]
6	0.72	2190 ± 20
9	0.77	1560 ± 10
13	0.81	No detonation

Analysing the results presented in Table 5, one can notice a substantial decrease in the detonation velocity of mixtures, along with the increase in the content of used alcohol. This correlation is caused by the absorption properties of AN granules. As mentioned earlier, the porous AN does not absorb the added alcohol completely, whose excess, from the point of view of chemical reactions occurring in the detonation wave, becomes an energy ballast causing a decrease in its speed and a decrease in detonability of the tested composition. With an ethan-1,2-diol concentration of 13%—corresponding to the ANED mixture's oxygen balance close to zero—the tested explosive did not detonate under the conditions of the experiment. This result confirmed the earlier assumption that the tested binary AN/fuel mixtures should contain 6% of the liquid component. Table 6 presents the results of measurements of detonation velocity of AN/fuel mixtures with the ratio of 94/6.

**Table 6.** Results of measurements of detonation velocity of AN/organic fuel compositions.

Explosive Composition	Organic Fuel	Density [g/cm <sup>3</sup> ]	Detonation Velocity [m/s]
ANFO	Fuel oil	0.70	1600 ± 40
ANPT	Propan-1,2,3-triol	0.73	1610 ± 40
ANPD	Propan-1,3-diol	0.70	1850 ± 30
ANPO	Propan-2-ol	0.68	1880 ± 20
ANE	Ethanol	0.68	2040 ± 10
ANBD	Butan-1,4-diol	0.71	1870 ± 10
ANED	Ethan-1,2-diol	0.72	2190 ± 20

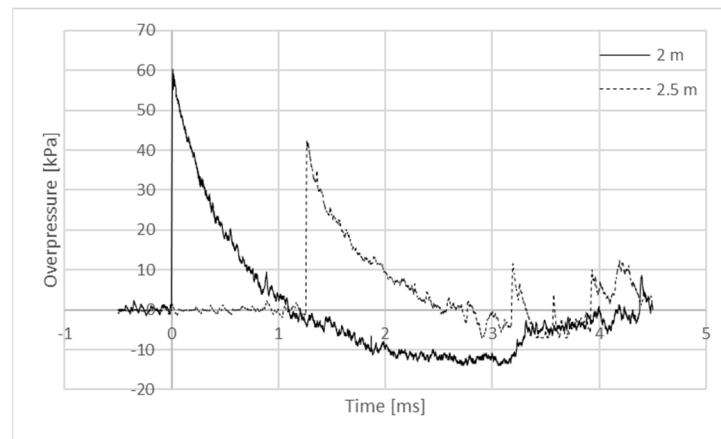
Of all the tested mixtures, the highest detonation velocity was obtained for a composition containing ethan-1,2-diol. This mixture has a high positive oxygen balance (+11.06%); therefore, tests of this material with aluminium were also carried out. Table 7 shows the results of detonation velocity measurements for mixtures in which different amounts of flaked aluminium were added to the oxidant/fuel system with a constant ratio of 94/6.

**Table 7.** Detonation velocity of AN/fuel compositions with the addition of flaked aluminium powder.

Explosive Composition	Aluminium Content [%]	Density [g/cm <sup>3</sup> ]	Detonation Velocity [m/s]
ANFO10	10	0.69	2320 ± 20
ANED5	5	0.69	2250 ± 20
ANED10	10	0.70	2420 ± 20
ANED15	15	0.71	2260 ± 20

### 2.3.2. The Results of Measurements of the Air Blast Wave Overpressure

For each of the tests, four registrations of the blast wave overpressure were obtained. Two histories are for the sensors located at a distance of 2 and 2.5 m. Figure 3 illustrates exemplary histories of air blast wave overpressure obtained for ANPD composition.



**Figure 3.** Air blast wave overpressure for ANPD composition.

The overpressure histories were approximated with a modified Friedlander equation. The obtained results of maximum overpressure and positive phase impulse were averaged. Measurements were made for two-component systems and, in the case of ethan-1,2-diol, with the addition of aluminium dust. Tables 8 and 9 present the determined characteristics of the air blast wave.

**Table 8.** Results of measurements of blast waves characteristics of AN/organic fuel compositions.

Explosive Composition	Overpressure at 2 m [kPa]	Specific Impulse at 2 m [Pa·s]	Overpressure at 2.5 m [kPa]	Specific Impulse at 2.5 m [Pa·s]
ANFO	47 ± 3	20 ± 2	30 ± 2	15 ± 1
ANPT	47 ± 3	20 ± 1	30 ± 1	15 ± 1
ANPD	53 ± 5	23 ± 2	35 ± 2	17 ± 2
ANPO	53 ± 7	23 ± 3	36 ± 2	19 ± 1
ANE	58 ± 2	25 ± 2	39 ± 2	20 ± 1
ANBD	48 ± 2	20 ± 1	33 ± 3	17 ± 1
ANED	55 ± 4	23 ± 2	36 ± 3	21 ± 1

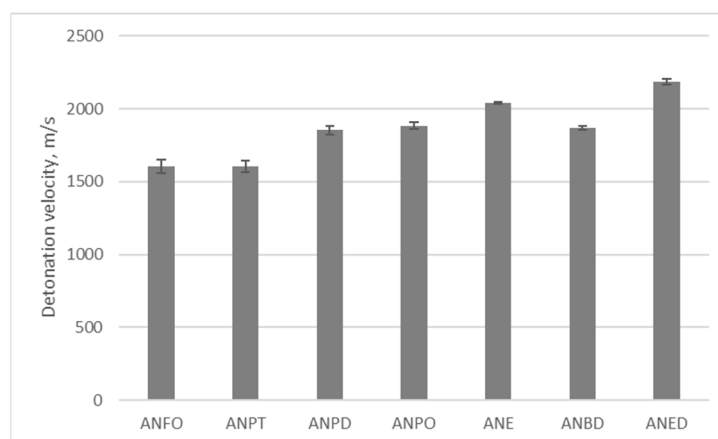
**Table 9.** Blast waves characteristics for ANFO and AN/ ethan-1,2-diol mixtures with an addition of Al<sub>f</sub>.

Explosive Composition	Al <sub>f</sub> Content [%]	Overpressure at 2 m [kPa]	Specific Impulse at 2 m [Pa·s]	Overpressure at 2.5 m [kPa]	Specific Impulse at 2.5 m [Pa·s]
ANFO10	10	70 ± 5	31 ± 3	48 ± 1	25 ± 1
ANED5	5	66 ± 4	28 ± 1	39 ± 3	20 ± 2
ANED10	10	75 ± 4	35 ± 3	45 ± 4	25 ± 3
ANED15	15	80 ± 1	35 ± 3	55 ± 3	32 ± 4

### 3. Analysis of Test Results

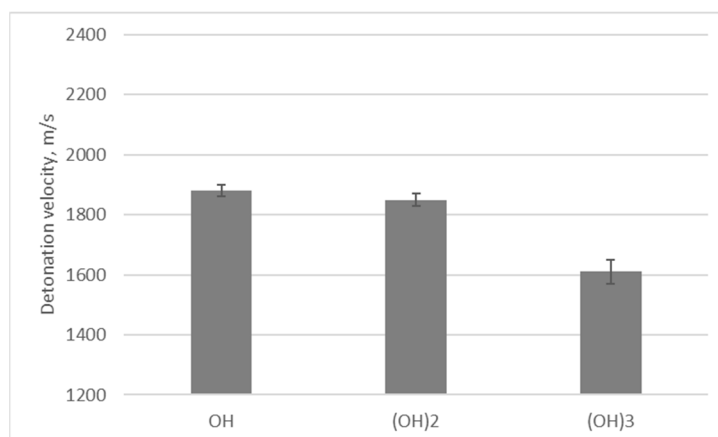
Figure 4 presents the summary results of the detonation velocity for the tested explosive mixtures. Similar or higher detonation velocity values were obtained for all the AN mixtures with alcohols, as compared to the classic ANFO mixture.

The alcohols used in the experiments have different structures and elemental composition of their molecules, which affects some physicochemical properties that can directly affect the value of the detonation velocity of the tested binary explosive mixtures. These parameters are oxygen balance, viscosity and flash point (Table 1).



**Figure 4.** The dependence of the detonation velocity of ammonium nitrate-based explosives on the type of alcohol added.

Some interesting correlations can be seen considering the structure of the molecules of the applied alcohols. Figure 5 shows the results of measuring the detonation velocity for mixtures of AN with alcohols with a constant carbon chain length (C3) and a variable number of hydroxyl groups (which corresponds to mixtures: ANPO, ANPD, ANPT).



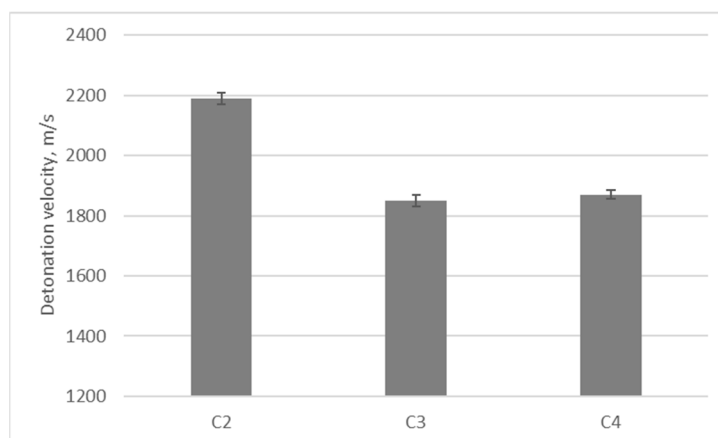
**Figure 5.** The dependence of the detonation velocity of the AN mixture with alcohols with different numbers of hydroxyl groups in the fuel molecule.

It can be observed that as the number of hydroxyl groups increases, the detonation velocity decreases. As shown in Table 1, the increase in the number of hydroxyl groups causes an increase in dynamic viscosity and alcohol ignition temperature. Simultaneously, the tested mixtures of alcohols with ammonium nitrate, along with the decrease in the number of hydroxyl groups, are more and more oxygen balanced (Table 3). Lower viscosity enables the alcohol to penetrate the porous oxidant granule better, increasing the surface area of the potential chemical reaction between the products of ammonium nitrate decomposition and the fuel. The lower flash point enables this reaction to start faster, and the more oxygen-balanced oxidant-combustible component provides a more significant thermal effect per volume unit of the mixture.

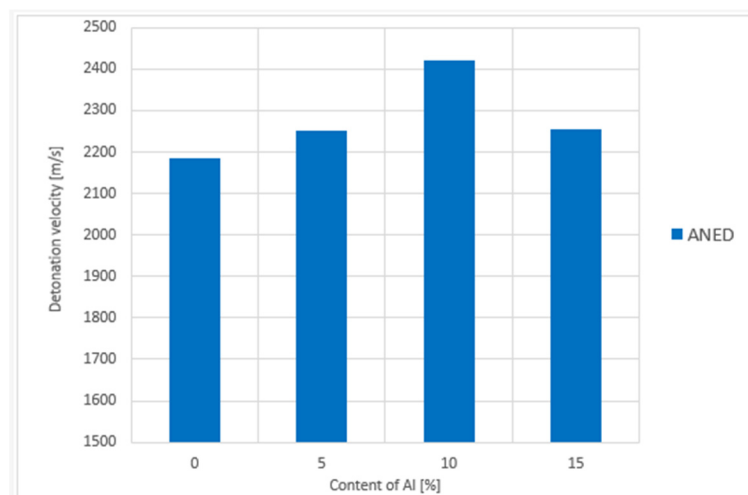
Figure 6 illustrates the dependence of the detonation velocity of tested mixtures with double hydroxyl groups (2OH) on the number of carbon atoms in the alcohol molecule (which corresponds to the mixtures: ANED, ANPD and ANBD).

As one can see, as the carbon chain length increases in the alcohol molecule, the detonation speed of the mixtures tested decreases. The alcohols compared in this case have similar flashpoints (Table 1), and their mixtures with ammonium nitrate are characterised

by relatively comparable oxygen balances (Table 3). In contrast, alcohols differ significantly in viscosities. The longer the molecule chain, the higher the viscosity (Table 1). The alcohol parameter that determines the velocity of detonation is its viscosity, which determines the explosive composition's homogenisation. The highest detonation velocities were obtained for a mixture of ethan-1,2-diol with ammonium nitrate. The ANED explosive mixture has a positive oxygen balance—11.06% (Table 3). Various amounts of flaked aluminium powder were added to ANED to balance this OB. The results of the detonation velocity of aluminised ANED are illustrated in Figure 7.



**Figure 6.** The dependence of the detonation velocity of AN mixtures with alcohols on the carbon chain length in a molecule.



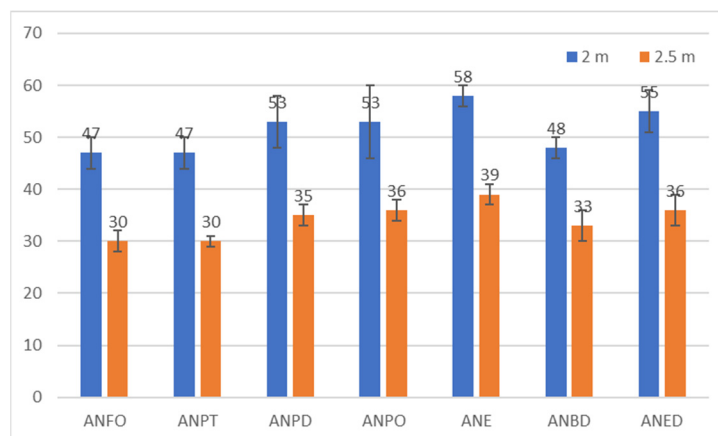
**Figure 7.** Dependence of detonation velocity of AN/fuel mixtures on the content of aluminium additive.

The highest detonation velocity was obtained for a mixture containing 10% flaked aluminium powder within the tested range of aluminium powder content. It had the oxygen balance equal to +1.06% (its closest to 0%). The obtained data testify to some aluminium reactivity in the chemical reaction zone of the detonation wave. The oxidation of aluminium is a highly exothermic reaction that contributes to the energy of the explosion.

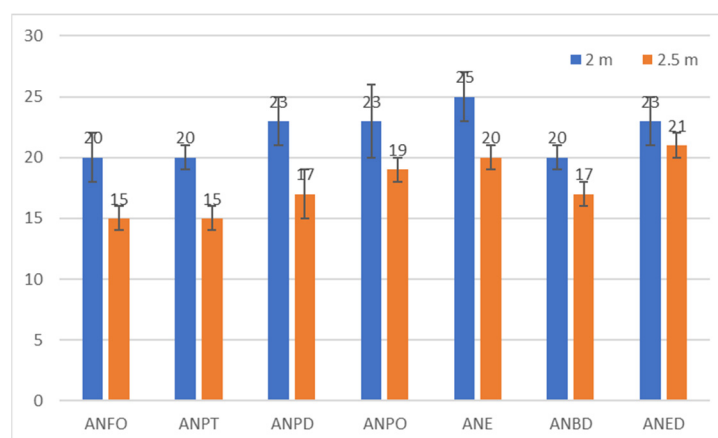
Above an aluminium powder content of 10% there is a decrease in the detonation velocity because the metallic addition becomes an energy ballast, taking away the heat from the reaction zone.



The same applies to the air blast wave characteristics generated by the explosion of charges of the explosive mixtures tested. The obtained results of their measurement and calculations are presented in Figures 8 and 9.



**Figure 8.** Dependence of maximum air blast wave overpressure on the type of organic fuel.

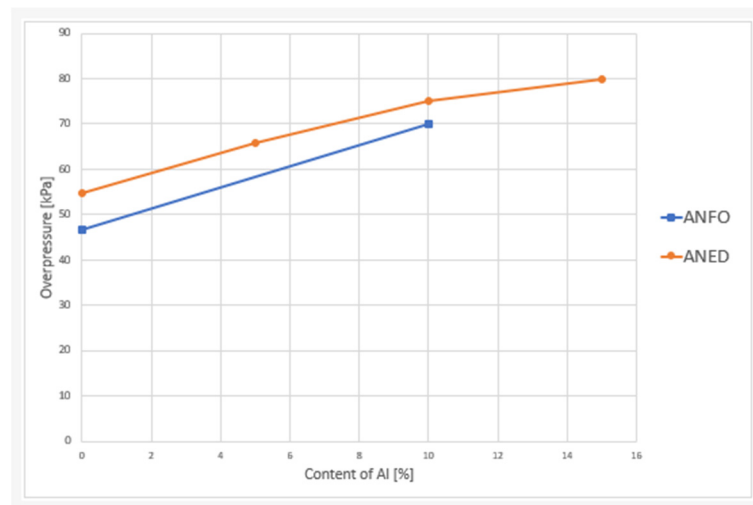


**Figure 9.** Dependence of the specific impulse on the type of organic fuel.

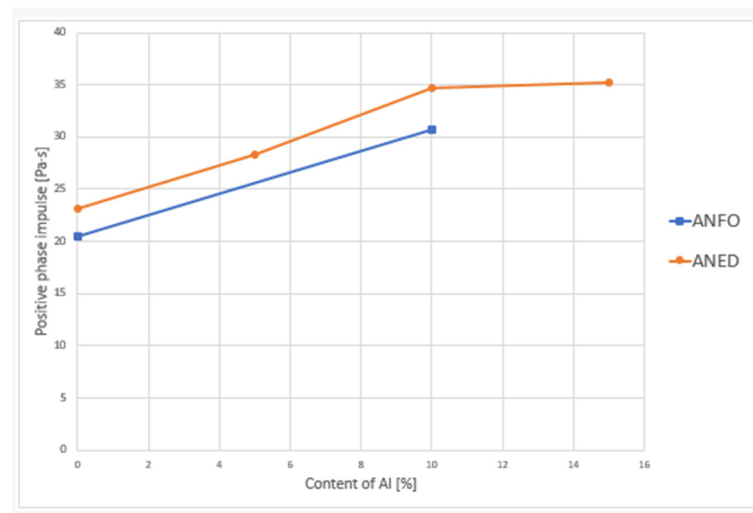
As can be seen in most measurements, the addition of alcohol to granular ammonium nitrate instead of fuel oil allows higher values of blast wave characteristics. Analysing the dependence of the impulse of the positive phase on the type of organic fuel, we can see that, compared to the classic ANFO mixture, the ANPT mixture has reached a comparable value for this parameter. Higher blast wave characteristics have been obtained for all other mixtures.

For the ANED mixture, additional measurements were carried out for materials with the addition of aluminium Al<sub>f</sub>. Comparative experiments were performed for classical ANFO. The test results are illustrated in Figures 10 and 11.

The data shown in the above graphs (Figures 10 and 11) show that increasing the aluminium content in the tested explosive compositions causes an increase in the detonation parameters. Simultaneously, it should be noted that materials based on ethan-1,2-diol obtained higher detonation parameters than classically used fuel oil-based explosives (ANFO). The increase in the parameters of air blast waves is caused by the burning of aluminium dust within ammonium nitrate decomposition products behind the detonation waves. A positive effect is also the reduction of the tested mixtures' critical diameter by the addition of aluminium powder characterised by a specific high surface, which is typical for explosives based on ammonium nitrate [11]. These factors have a positive impact on the conversion degree of oxidant-flammable component explosives.



**Figure 10.** Dependences of blast wave overpressure on the aluminium content in AN/fuel mixtures with the addition of aluminium at a distance of 2 m from the load.



**Figure 11.** Dependences of specific impulse on the aluminium content in AN/fuel mixtures with the addition of aluminium at a distance of 2 m from the load.

#### 4. Conclusions

The presented series of experiments showed that replacing fuel oil with alcohols in ANFO explosives increases their detonation parameters. The main factors that contribute to this are lower viscosity and flashpoint of the tested alcohols as compared to oil. Lower viscosity results in better penetration of the liquid component into the ammonium nitrate granule, resulting in a potential reaction zone between oxidation decomposition products containing oxygen in the molecule and alcohol. The effect of this phenomenon is increased conversion. However, lower viscosity and the ignition temperature of alcohols negatively affect the useful properties of explosives. The low viscosity allows for a high degree of desorption of the liquid component from the oxidant granules. The low flash point creates the risk of ignition of alcohol vapours, which can initiate explosive exothermic reactions in an explosive mixture in extreme cases. Therefore, the results of the experiments presented in this paper have mainly theoretical value.

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B.K.; visualisation, J.P., A.K., A.M. and B.K.; supervision, J.P., A.K., A.M. and B.K.; funding acquisition, B.K. All authors have read and agreed to the published version of the manuscript.

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