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Research paper / Praca doświadczalna

Explosive potential of energetic mixtures based on hydrogen peroxide *Potencjał wybuchowy mieszanin energetycznych zawierających nadtlenek wodoru*

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Abstract. *The explosion and detonation of energetic compositions based on hydrogen peroxide (H_2O_2 , HP) is investigated. Fuels with different oxygen balance were considered in the mixture with HP/ methanol, ethylene glycol, glycerine ethanol. Detonation performance at a wide range of reciprocal HP/fuel concentrations was examined. Heats of explosion at constant volume, detonation velocity, as well as volume of gaseous products of reaction were estimated in thermochemical evaluations. The modification of explosive properties of the high-energetic CHNO material by addition of hydrogen peroxide, was also investigated. To represent CHNO explosives, nitromethane was considered. In the performed analysis, aqueous solutions of hydrogen peroxide were considered with the aim of obtaining the appropriate fuel/HP/water ratios to predict potential explosive compositions.*

Streszczenie. *W pracy przedstawiona została analiza parametrów wybuchu i detonacji mieszanin energetycznych zawierających nadtlenek wodoru (H_2O_2 , HP). Jako dodatki rozważane były niewybuchowe materiały o ujemnym bilansie tlenowym. Rozpatrzone zostały dwie grupy paliw, metanol, glikol etylenowy i gliceryna o umiarkowanie ujemnym bilansie tlenowym oraz alkohol etylowy o zdecydowanie ujemnym bilansie tlenowym. Wybuchowe i detonacyjne właściwości badanych mieszanin paliwo/HP badane były w szerokim zakresie wzajemnych zmian stężenia składników. Ciepło wybuchu w stałej objętości, prędkość detonacji oraz objętość gazowych produktów przemiany określone były za pomocą obliczeń termochemicznych. Rozpatrzone zostały również wpływy dodatku HP do materiału wybuchowego z grupy CHNO. Jako przykładowy materiał z grupy CHNO rozpatrzony został nitrometan. Przyjmowano zastosowanie HP w roztworze wodnym. Przedmiotem prowadzonych analiz było określenie zakresów stężeń, dla których mieszaniny paliwo/HP/woda będą odpowiednie do stosowania w ładunkach wybuchowych.*

Keywords: *hydrogen peroxide, energetic compositions, explosive performance*

Słowa kluczowe: *nadtlenek wodoru, mieszaniny energetyczne, parametry detonacji*

Nomenclature:

B_T	oxygen balance [%]
$C_{(s)}$	concentrations of elemental carbon [g/kg]
D	theoretical detonation velocity [m/s]
V_{gas}	volume of products in gaseous phase [m ³ /kg]

Q_v	detonation energy at constant volume [MJ/kg]
μ	molecular mass [g/mol]
ρ_0	density [kg/m ³]

1. Introduction

Hydrogen peroxide (H₂O₂, HP) has many applications as either a monopropellant or an oxidizing agent in hypergolic mixtures [1-5]. In addition to its use as a liquid propellant, possible applications as an oxidant in combustion systems, in combustion engines, are indicated [1]. In view of the advantages, such as low vapour pressure, high temperature of decomposition products, good performance comparable to that of liquid oxygen [2], HP attracts an interest in using it as a satellite or rocket propellant [2, 3]. In view of its high reactivity, the safety aspects of handling, transportation and use of HP are studied. Based upon HP properties, case histories and experimental investigations, the types of possible hazard and necessary protection methods are recognised [4, 5].

The suggestion of considering HP as a component of liquid explosives [1] is of new significance in the contemporary need for “green energetics” [3, 6]. It is anticipated that HP-based explosives could be used like current ammonium nitrate (AN)-based mining explosives, that is, sensitised while being loaded into the blast-hole [7]. In fact, in the last couple of years, the use of HP to formulate explosives for use in mine blasting has been extensively studied [8-12]. Examples of formulations of these explosives are given by Nikolczuk *et. al.* [12], where mixtures of 67-77% HP, 15-5% AN, 13.9% glycerine, 13.9% guar gum and 1% glass microspheres were investigated. The use of matched mixtures is necessary to satisfy technological, efficacy and safety reasons. In modelling studies undertaken in this work, HP performance is considered in the presence of only one chemical substance. Then, by considering the influence of a unique additive, it appears easier to explain the HP behaviour in a wide range of its concentrations.

In the paper, explosive parameters of HP mixtures with fuels having a different oxygen balance (B_T), are investigated. Thermodynamic calculations are performed to determine values of detonation velocity, magnitude of explosion energy, specific volume of products in the gaseous phase, concentration of elemental carbon (soot). The applied method of minimizing the thermodynamic potential of reacting mixtures ensures the consideration of a wide list of possible chemical substances to be present in explosion and detonation products [13]. The presence of components in gaseous, liquid or condensed phases in detonation products is appraised.

The efficacy of the employed method of calculation was verified by comparison of evaluated results with experimental values of detonation velocities and pressures [14]. The obtained results indicate concentration ranges in which compositions of HP/non-explosive (fuels) may find a practical application.

2. Components

Two groups of fuels were considered for the explosive formulations using HP as the oxidiser. One group was made of alcohols having an increased number of oxygen atoms in the molecule and therefore a different B_T . These alcohols were:

- methanol and ethanol (one oxygen atom),
- ethylene glycol (two oxygen atoms),
- glycerine (three oxygen atoms).

The second fuel group was in fact a material that is an explosive itself and could produce nitrogen oxides (NO_x), *i.e.* nitromethane. The goal in this case was to improve its B_T and reduce the amount of toxic substances like CO, NO_x and others that are to be found in detonation products. Nitromethane was considered as a representative of CHNO group of explosives.

Two types of HP solution were used in the formulations – 60% (HP60) and 90% (HP90). The specifics of the additives are shown in Table 1 while in Table 2 the characteristics of HP and its water solutions are presented.

Table 1. Fuels used in the formulations

Species	Chemical formula	μ [g/mol]	B_T [%]	ρ_0 [kg/m ³]	$\Delta_f H(298.15)$	
					[kJ/mol]	[kJ/kg]
Ethanol	C ₂ H ₅ OH	46.0688	-208.4	789.3	-277.9	-6032
Methanol	CH ₃ OH	32.0420	-149.8	791.0	-238.5	-7443
Ethylene glycol	C ₂ H ₆ O ₂	62.0682	-128.9	1109.0	-454.3	-7319
Glycerine	C ₃ H ₈ O ₃	92.0944	-121.6	1261.0	-666.1	-7233
Nitromethane	CH ₃ NO ₂	61.0402	-39.3	1139.0	-112.55	-1844

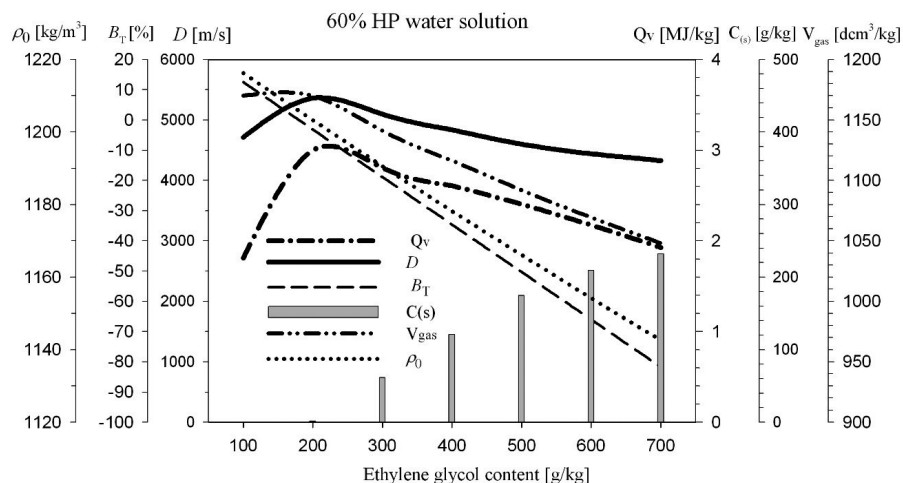
Table 2. HP/water solutions

Species	Hydrogen [mol/kg]	Oxygen [mol/kg]	$\Delta_f H(298.15)$		B_T [%]	ρ_0 [g/cm ³]
			[kJ/mol]	[kJ/kg]		
HP	58.7983	58.7983	-187.8	-5520	47.0	1.49
HP90	64.0202	58.4693	–	-6553	42.3	1.40
HP60	79.6859	57.4824	–	-9649	28.2	1.25

The CH materials consisting of carbon and hydrogen only, appear to be not the most suitable for use as fuels in explosive compositions with HP as they are highly oxygen negative and as a result toxic fumes (CO for example) could be easily formed during the detonation process. As a rule, the oxygen balance of the resultant mixture will be highly negative, meaning that the formation of non-contributory, toxic substances in explosion products is unavoidable.

3. Explosive performance of HP/fuel mixtures

Methanol, ethylene glycol and glycerine differ only slightly in their enthalpies of formation (Table 1). Ethylene glycol was chosen to represent this group of fuels. Its mass density and B_T are of immediate value. The detonation's theoretical calculations for ethylene glycol and HP60/HP90 mixtures are presented in Figures 1 and 2, respectively.

**Figure 1.** Explosive parameters of 60% HP mixtures with ethylene glycol

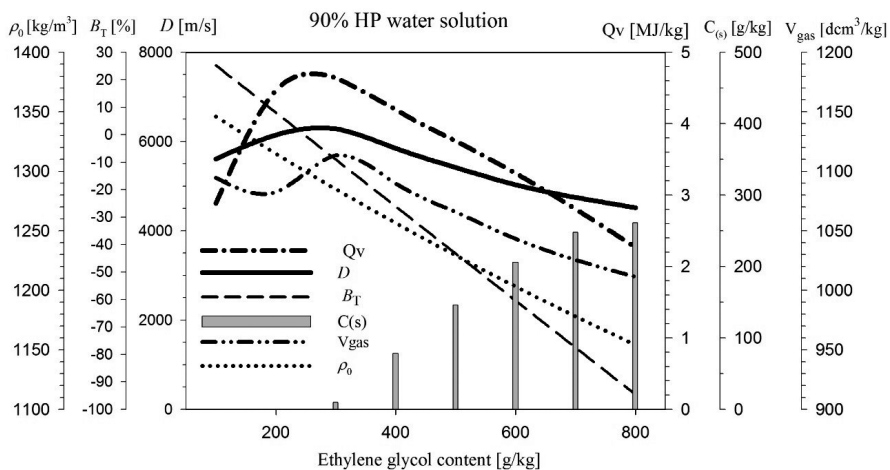


Figure 2. Explosive parameters of 90% HP mixtures with ethylene glycol

The relationship between D and Q_v is presented. In rock blasting, the explosion energy at constant volume becomes the decisive parameter which characterizes the output of the explosive. On the other hand, in some cases the considered mixtures may detonate in a non-ideal manner. Then, the energy evolved in the detonation zone (before the C-J point) is different from the total energy produced after completion of chemical reactions at constant volume.

The plot for HP90 with ethylene glycol shows that the oxygen balanced mixture (around 250-300 g/kg ethylene glycol) has a Q_v of more than 5 MJ/kg. In the case of mixtures that are not oxygen balanced, *i.e.* having 100 to 600 g/kg of ethylene glycol, the Q_v is still above 3.0 MJ/kg. In the case of HP60 with ethylene glycol mixtures, theoretically only 3 MJ/kg are released in an oxygen balanced mixture (Fig. 1), which means around 40% less energy when compared with HP90. It is observed that for both HP90 and HP60, the amount of gas released (V_{gas}) appears to be quite similar. The high specific volume of gaseous products seems to be the dominant feature of mixtures containing HP. The detonation's theoretical calculations for the ethylene glycol/HP90 mixture with ethanol are presented in Figure 3.

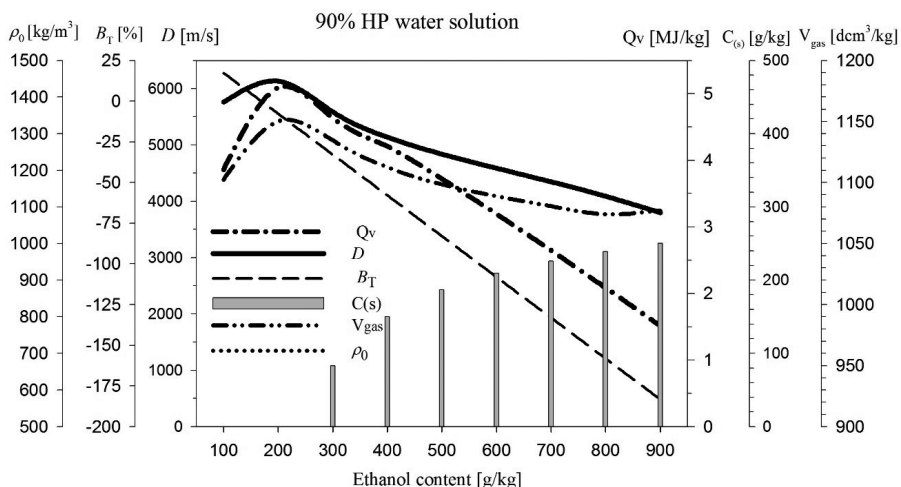


Figure 3. Explosive parameters of 90% HP mixtures with ethanol

Ethanol, due to its highly negative oxygen balance, requires more HP to form a mixture with a final B_T close to zero. Therefore, only the addition of HP90 was considered in the calculations. Plots of HP90 solution mixed with ethylene glycol and ethanol (Figs. 1 and 3, respectively) display a visible rise of hard black carbon (soot) concentrations in the latter, from 300 g/kg at higher concentrations.

Nevertheless, the obtained results show that even for fuel with an B_T lower than -200% , the promised magnitudes of explosive energy will be achieved. The detonation energy is nearly the same (around 3 MJ/kg), whether the fuel is ethylene glycol or ethanol, in the concentration range from 100 to 600 g/kg. It is important to note that the detonation of the mixtures must be tested practically in a detonation facility to confirm detonation. The conclusion that, with a lowering of B_T an increase of concentration of elemental carbon occurs, may be extended to other possible additives in HP-based mixtures.

4. Explosive performance of HP compositions with CHNO high-energetic materials

The theoretical detonation calculations conducted in this study provide the basis for a practical application of HP/ethylene glycol or HP/ethanol mixtures. An interesting alternative to consider is the influence of energetic materials, like nitromethane, in mixtures with HP. The B_T of nitromethane is negative (Table 1) so when it detonates, elemental carbon and CO could be formed. Therefore, it is expected that by adding HP, the detonation parameter could be improved (D , *etc.*) and the evolution of non-desired substances (CO, C, *etc.*) is reduced or eliminated. Calculated detonation parameters of the HP mixtures with nitromethane are presented in Figure 4.

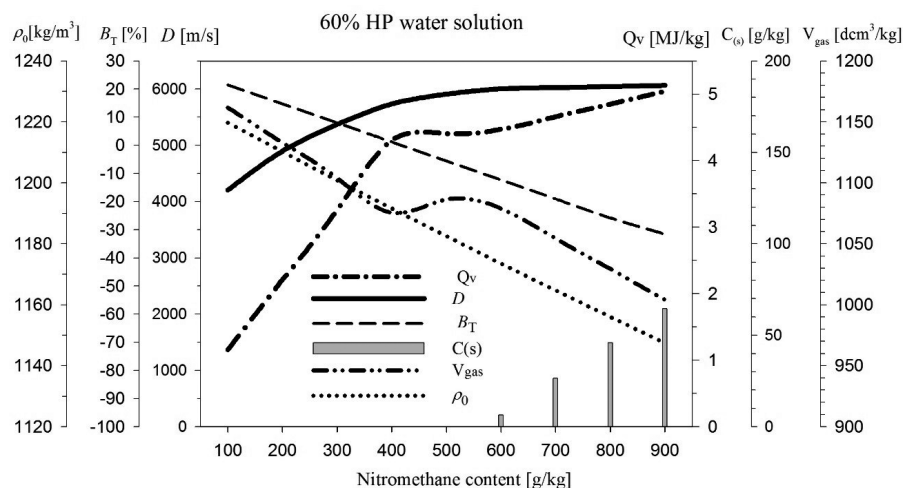


Figure 4. Explosive parameters of 60% HP mixtures with nitromethane

Calculations show that by adding HP, a considerable shift in conditions at which elemental carbon is formed. If HP concentration exceeds 40 wt.%, theoretically no soot is formed in the explosion products. However, HP addition to nitromethane brings no remarkable improvement in detonation parameters (D and Q_v). By increasing the concentration of HP a reduction in the carbon content per unit mass of explosive occurs. Then the role of energy delivery is passing from CO, CO₂ to H₂O. Detonation velocity stays at nearly the same level, up to 50/50 nitromethane/HP60 compositions. The important advantage to be noted is the considerable rise in the amount of gaseous products. V_{gas} of 50/50 nitromethane/HP60 mixtures exceeds of 1.050 m³/kg.

5. Conclusions

Theoretical thermo-chemical calculations for the detonation of energetic compositions based on HP mixed with fuels were carried out, in concentrations of 60 and 90 wt.%. Fuels used in the calculations were methanol, ethylene glycol and glycerine, with B_T ranging from -120 to -208% . Also, the possible influence of HP addition on the detonation parameters of a CHNO type explosive was analysed. Nitromethane was chosen as a CHNO representative.

Detonation velocity, heat of explosion at constant volume, volume of products in gaseous phase as well as formation of elemental carbon in transformation products, were estimated using the above theoretical thermo-chemical calculations. The efficacy of the employed method of calculation was verified by comparison of evaluated results with experimental values of detonation velocities and pressures. Explosives of mass density varying from 1800 to 1000 kg/m^3 with wide ranges of B_T , were examined.

Significant values of detonation energy were attained by addition of the first group of fuels to HP90. An explosion energy reaching 5 MJ/kg was obtained for a B_T balanced mixture. Heat of explosion above 3 MJ/kg was obtained for mixtures containing 100 to 600 g/kg of the ethylene glycol in mixtures with HP90 (these mixtures had a very positive or negative B_T). The efficiency of mixtures with HP60 was lower than HP90. An explosion energy up to 3 MJ/kg may be obtained in oxygen balanced compositions, which contain 250 g/kg of ethylene glycol.

In the case of HP90 with ethanol, a fuel with a more negative B_T , the theoretical thermo-chemical calculations have favourable explosion parameters. The magnitude of the heat of explosion of HP90/ethanol mixture reaches a detonation energy of 5 MJ/kg with ethanol contents close to the B_T balanced mixture. As far as the $C_{(s)}$ is concerned, HP90/ethanol mixtures produce a larger amount than HP/ethylene glycol mixtures.

The important feature of the investigated mixtures is the relatively large amount of substances in the gaseous phase, produced by explosion and detonation. In this parameter, no differences between mixtures based on HP60 or HP90 with fuels occur. The volume of gaseous products reaches 1.100 m^3/kg or more, as a rule. The high specific volume of gaseous products seems to be a specific feature of mixtures containing HP. Introduction of HP60 into highly energetic materials such as nitromethane, brings no noticeable improvement in detonation (D) or explosion (Q_v) parameters.

Nevertheless, three positive effects may be obtained with the inclusion of HP in nitromethane:

- a reduction in the formation of elemental carbon (soot),
- an increase in the volume of gaseous products,
- a reduction in the concentration of possibly harmful chemical substances (CO , *etc.*) in the detonation explosion products.

The practical application of the mixtures in this document needs further investigation to prove their potential rock breaking characteristics and the safety aspects of transport, storage and use.

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