

Article

Thermodynamic Assessment of the Impact of Selected Plastics on the Energy Parameters of Explosives

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Abstract: Global economic development and the associated increase in consumption increase the demand for plastics. The result of these changes is the increase in the share of this group of used plastics in the structure of household waste. An innovative way of managing plastic waste is to use it as a component of a high-energy material. According to the conceptual assumptions, some plastics introduced into the structure of an explosive (Ex) in appropriate amounts can improve the energy parameters of a high-energy material. Modification of the composition of the explosive causes a change in its explosive and operational parameters. It also becomes necessary to develop a method of introducing an additional component. Computer programs for thermodynamic calculations are a tool for modeling the predicted energy parameters of an explosive. The performed simulations and modeling allow for the selection of appropriate compositions for laboratory and “in situ” tests. This reduces the number of field tests performed. This enables the more effective design of new explosive compositions. The use of waste plastics as a corrector of explosive properties may also be pro-environmental in nature through the use of a detonation method of their disposal and will reduce the cost of manufacturing the product. The conducted analyses showed that for three ANFO-type explosives containing 2% polyethylene—PE 2.0, 1% polypropylene—PP 1.0 and 1% polyurethane—PU 1.0, obtained energy parameters similar to ANFO and qualitatively and quantitatively similar structure of post-detonation gases.

Keywords: thermodynamic analysis; ANFO explosives; waste plastics; detonative disposal



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1. Introduction

The production of plastics has grown exponentially in just a few decades. In 1950, it amounted to 1.5 million tons and in 2018 as much as 359 million tons per year worldwide. The amount of plastic waste has also increased in parallel. Its accumulation is an environmental problem. This applies to both synthetic polymers and their composites—plastics that are biostable and can persist in nature for hundreds of years [1]. Plastics are distinguished by many advantages, such as durability, ease of molding and resistance to corrosion. They are also very good electrical insulation, and in addition, they can be easily dyed in various colors. All these advantages have caused plastics to be used in our everyday life very often.

Every year around 250–300 million tons of synthetic polymers and plastics are produced in the world [2]. More than 90% of all plastic products are made of mainly: rubber (latex), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET). Only some, 30–35%, of this waste, mainly PET bottles, rubber tires and some other polymer products, are recycled in the world. However, about 65–70% (150–170 million tonnes) of biostable polymers and plastics are thrown away every year. In this way, the environment is polluted—landfills occupy huge areas and distort the landscape. The pollution of water reservoirs and oceans with such waste is also a problem.

Up to 10 million tons of plastic are dumped into the ocean every year. Currently, over 7 billion tons of biostable plastic waste have been collected in the world [3].

In 2020, global plastics production was around 367,000,000 tonnes [4]. The share of PE and PP in the structure of the global production of plastics is 46% [5]. They also occupy a dominant position in the EU, including Poland. Table 1 shows [6–8] the production of selected plastics in 2018–2020.

Table 1. Comparison production of selected plastics in the EU and Poland [6–8].

Product Type	Production (Thousand Tonnes)					
	EU			Poland		
	Year					
	2018	2019	2020	2018	2019	2020
Plastic in primary forms of which:	61,800 ¹⁾	57,900 ¹⁾	55,000 ¹⁾	3456	3627	3682
Polyethylene	12,310.1	11,733.4	11,643.2	346	383	348
Polypropylene	10,755.5	10,471.5	10,090.7	287	351	351
Polymers of styrene	5590.0	5708.6	5121.1	146	175	168
Polyvinyl chloride, not mixed with other substances	5311.7	5160.1	4953.9	255	243	295
Plasticized polyvinyl chloride mixed with any other substance	917.9	880.6	726.5	108	107	94.2
Polyamides	2763.9	2580.8	2259.4	194	192	189

Note: ¹⁾ [4].

The table clearly shows that over the last 3 years (despite the period of the COVID-19 infectious disease pandemic), the production of plastics did not show a drastic decrease.

Increasing the scale of use of products made of plastics has led to an increase in the amount of waste. Thus, the risk of their improper management and negative impact on the environment increases—especially since, compared to other types of waste, recycling rates for plastic waste remains low.

According to the Organization for Economic Co-operation and Development (OECD), around 79 million tons of plastic waste were directly released into the environment in 2019: into the soil, oceans and by burning in open pits or in illegal landfills. This corresponds to more than a fifth of the total amount of plastic waste in the world. A glimpse of how this waste is dealt with is shown in Figure 1, which shows how it was disposed of in 2019. Only 9% of global plastic waste was recycled [9].

Plastic waste management consists of reducing, managing and limiting the amount of waste from its production to final disposal.

Traditional plastics are resistant to biodegradation and, therefore, cannot be landfilled. They should be disposed of by other methods. Two approaches are preferred (Figure 2): conventional and innovative. Conventional technology is a method of reducing the amount of waste by using various disposal techniques that can be implemented (chemical processing or material recycling) [10–14].

Innovative technologies include, among others, energy methods (gasification or co-combustion) that enable obtaining energy [15–20].

One of the most progressive concepts for solving waste problems is the "Zero Waste" strategy. It covers many different activities for sustainable waste management; it concerns waste reduction, repair, reuse and recycling [21,22]. The Zero Waste concept focuses on the waste hierarchy (Figure 3) and complies with the EU directive [23].

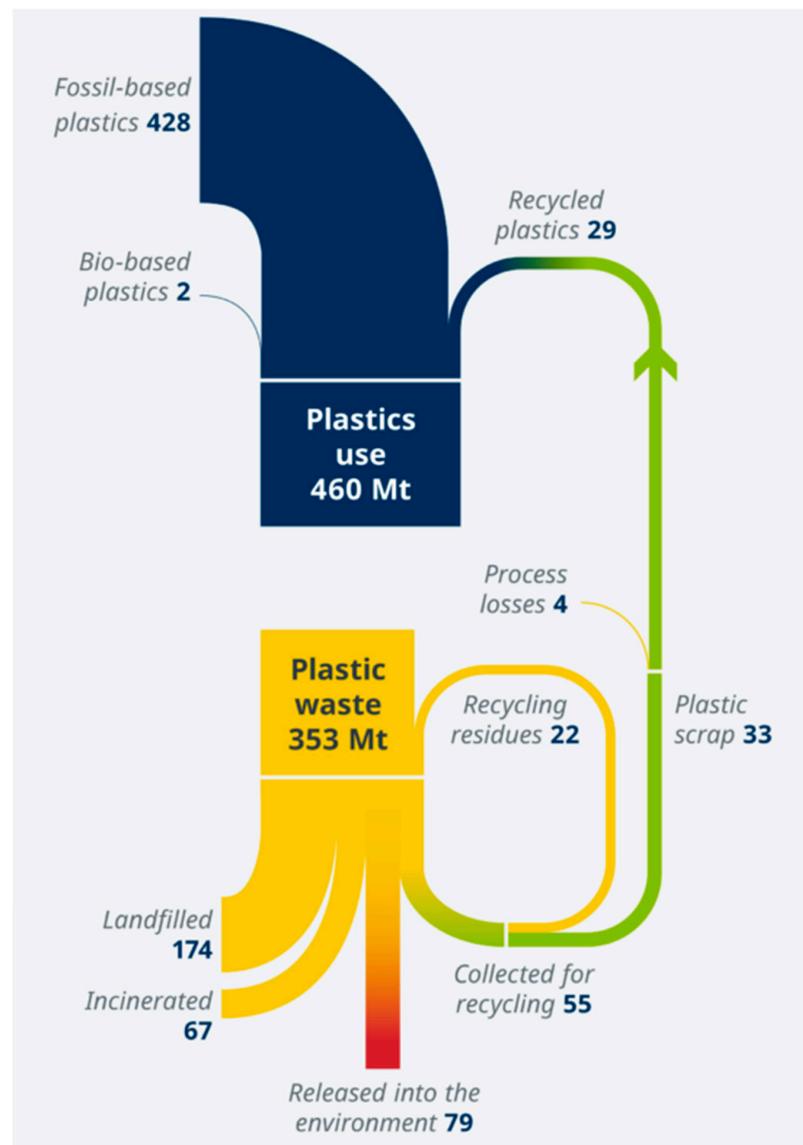


Figure 1. Structure of plastic waste and its management in millions of tons (Mt) [9].

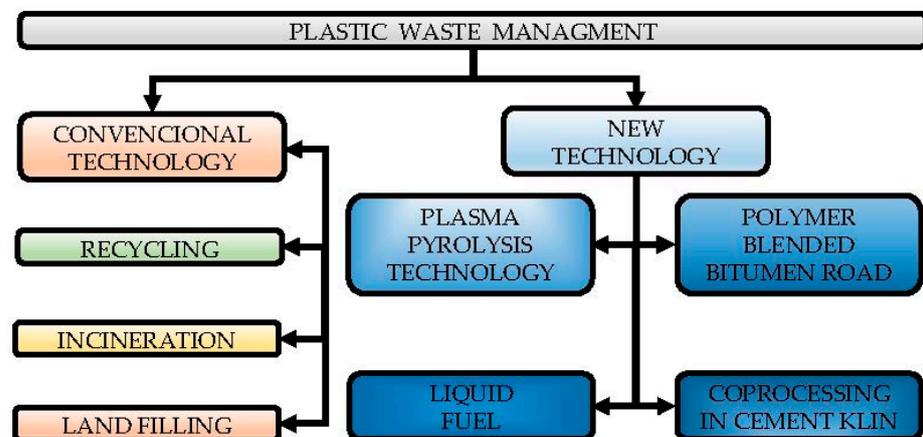


Figure 2. Plastic Management Flowchart [10].

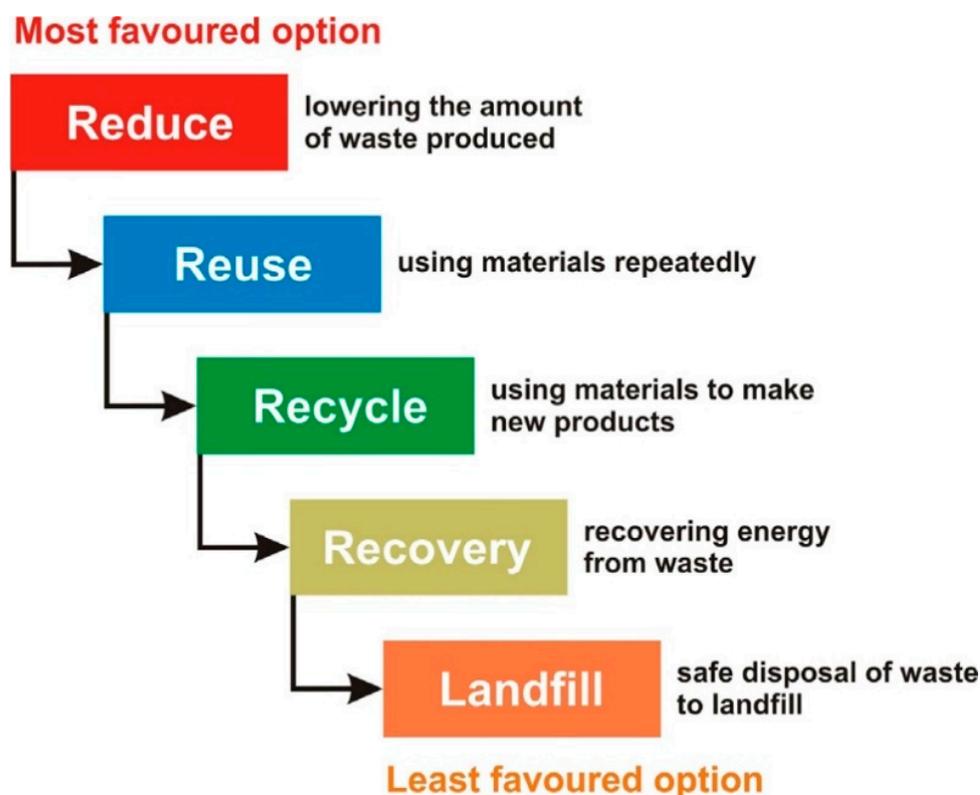


Figure 3. The Waste Hierarchy [22,23].

Many major cities around the world (Adelaide, San Francisco and Stockholm) implement toward zero waste, and many countries have introduced "Zero Waste Commitments". These include the USA (California), Canada (Nova Scotia), Australia, New Zealand, Lebanon, Taiwan and China [24].

Some of the radical methods of disposal of plastic waste are various types of incineration. Due to its properties (high calorific value), this waste is a beneficial source of energy (Table 2).

Table 2. Heat of combustion and calorific value of some synthetic polymers.

Sample	Q *, MJ/kg	Q **, MJ/kg	Ref.
Rubber	45.0	42.4	[25,26]
PE	47.1	44.6	[27]
PP	47.1	44.6	[27]
PS	41.7	40.0	[27]
PMMA	26.8	25.0	[27]
PET	24.1	23.2	[27]
PVC	22.7	19.2	[25,26]
PA-6	32.8	30.2	[27]

* HHV (High-Heating Value); ** LHV (Low-Heating Value).

The neutralization of waste will consist of using it as additives in products that generate extreme temperatures during combustion. Such possibilities are created by the detonation of explosives (Ex). Simple two-component mixtures used for civilian purposes are ANFO (Ammonium Nitrate Fuel Oil) explosives—nitrates are an important group of explosives. Attempts to modify their chemical composition with various additives seem reasonable and technologically simple. Such actions have already been taken with the use

of other additives, correcting the properties of explosives [28–32]. It is also possible to utilize some of the waste plastics this way. The susceptibility of ANFO-type explosives to the modification of the base chemical composition by the use of additional ingredients and the great variety and chemical complexity of waste plastics gives great opportunities to correct the thermodynamic properties of high-energy material. Optimal benefits are possible when three conditions are met:

- energy efficiency (improvement or maintenance of performance parameters similar to ANFO),
- environmental impact (use of the largest possible amount of plastics in terms of weight for the production of explosives),
- cost-effectiveness (increasing the amount of waste plastics in the MW structure reduces the amount of more expensive basic components: ammonium nitrate and oil, thus reducing the cost of production)

2. Materials and Methods

2.1. Characteristics of an ANFO-Type Explosive

Civil explosives are commonly used in mining for rock excavation and for engineering purposes (mainly demolition works and demining). It is the most economically viable way of obtaining rock and energy resources. Due to the low cost of production, the small amount of components needed for production and their easy availability, ANFO is very popular; it is a mixture of granulated ammonium nitrate and, most often, diesel fuel.

Ammonium nitrate, the main ingredient of ANFO, is an oxidant, has a positive oxygen balance of +20% and a low detonation temperature of about 1500 °C. It is hygroscopic and lacks water resistance, which is a disadvantage. Various forms of saltpeter are used for the production of nitrates. The most advantageous property of microporous granulated nitrate is its high sorption capacity. This feature makes it easy to combine with the oil and homogenize the ANFO ingredients.

The oil acts as a combustible component; it increases the specific heat of MW. Due to the low oxygen balance (about −300%), it cannot be used in quantities greater than about 10%. ANFO explosives are used in loose form, and are sold in bags for hand-loading. Most often in opencast mining, they are produced by mixing and loading systems at the place of their use. These devices have an open structure, thanks to which it is possible to expand them, if necessary, with additional chambers (e.g., with the addition of powdered plastics). It is technically possible to mechanize the production process of modernized ANFO-type explosives. Despite the shortcomings of ANFO, it is often used in rock mining for blasting. Although ANFO may seem technologically obsolete compared to more modern emulsion explosives, due to its numerous advantages, they are and will be used for mining purposes. Thus, modifying their chemical composition or modernizing them with additives seems reasonable and prospective.

2.2. Characteristics of waste plastics

The chemical composition of plastics is mostly a combination of carbon and hydrogen. These elements are also fundamental in the construction of explosives. Oxygen, nitrogen and chlorine are sometimes present in the structure of the polymer:

- polyethylene (PE): $[-CH_2 - CH_2-]_n$
- polypropylene (PP): $[-CH_2 - CH(CH_3)-]_n$
- polystyrene (PS): $\left[\begin{array}{c} -CH_2 - CH- \\ | \\ C_6H_5 \end{array} \right]_n$
- polyamide: $\left[\begin{array}{c} -NH- (CH_2)_i - N - C - (CH_2)_i - C- \\ | \quad || \quad || \\ H \quad O \quad O \end{array} \right]_n$ polyamide i $\left[\begin{array}{c} -NH- (CH_2)_k - N- C- \\ || \\ O \end{array} \right]$ polyamide k

- polyvinyl chloride (PVC): $\left[\begin{array}{c} -\text{CH}_2 - \text{CH}- \\ | \\ \text{Cl} \end{array} \right]_n$
- polyurethane (PU): $\text{OCN}- \left[\begin{array}{c} -\text{R}' - \text{N}- \text{C}-\text{O}-\text{R}'' - \text{O}- \text{C}-\text{N}- \\ | \quad || \quad \quad \quad || \quad | \\ \text{H} \quad \text{O} \quad \quad \quad \text{O} \quad \text{H} \end{array} \right]_n - \text{R}' - \text{NCO}$

Plastic [33–35] is an umbrella term for many different resins, but only thermoplastic resins are recyclable. Thermosetting plastics (duroplastics) cannot be recycled. Thermoplastic resins are linear polymers (containing a single chain of monomers) and branched polymers (linear with side chains). Thermoplastic resins account for 80% of the plastics produced and tend to soften when exposed to heat. The basic feature of plastics is their modulus of elasticity, which determines their direction of application. Depending on its value, the following division is used:

- up to 700 MPa—soft plastics,
- 700 to 7000 MPa—semi-rigid plastics,
- over 7000 MPa—rigid plastics.

The chemical structure and physical properties determine the direction of polymer application. Common applications of the analyzed plastics include:

- dense (rigid) polyethylene—high-density HDPE (PE-HD): for the construction of pipelines, fuel tanks, bottles, toys, thin bags and “rustling” foil,
- thin (soft) low-density polyethylene (LDPE) (PE-LD): for the production of containers, bags, pouches (“non-rustling”) and film tapes,
- polyethylene terephthalate (PET): for the production of 1.5- and 2-liter beverage bottles, and recently also 0.33-liter bottles, carpets and food containers,
- polypropylene (PP): for automotive components, fibers, some batteries and food containers,
- polystyrene (PS): most often found in the form of expanded polystyrene for the production of insulation boards for the construction industry, packaging for various products, including dairy products, mugs, cups and film cassettes,
- polyvinyl chloride (PVC): for window frames, floors, cable insulation, bottles, medical devices and film cassettes,
- polyurethane (PU): coatings, finishes, gears, membranes, cushions and mattresses.

Thermosetting resins (e.g., PU polyurethane) are cross-linked polymers (having two or more chains connected by side chains). They account for the remaining 20% of plastics produced. As a result of hardening, they cannot be melted or molded again. This makes them difficult to recycle.

2.3. The EXPLO5 Computer Program

The EXPLO5 software, version V6.06.02, was used to calculate the thermodynamic parameters. The EXPLO5 program can be used to calculate the energy properties of various mixtures. Calculations are based on chemical formulas, heat of formation and density. The program has a large database of ingredients and products, thanks to which it is possible to model energy parameters even for mixtures with a complex composition.

The gas state equation—BKW (Becker–Kistiakowsky–Wilson) was used for the calculations.

$$\frac{pV}{RT} = 1 + xe^{\beta x} = f(x) \quad (1)$$

where:

V —volume of gaseous products,

$$x = \frac{K}{V(T + \theta)^\alpha} \quad (2)$$

$$K = \kappa \sum_{i=1}^N x_i k_i \quad (3)$$

where:

k_i —covolume of i -th detonation product,

$x_i = n_i/n_T$ (mol fraction of i -th detonation product),

$\alpha, \beta, \kappa, \theta$ —adjustable constants.

In addition, the equation of state of the condensed phase—incompressible, and the equation of the calculation method—minimization of free energy, were used for the calculations. The calculations were carried out for the options set in the program: main products. The following constant values were used for the calculations:

$\alpha = 0.5,$

$\beta = 0.38,$

$\kappa = 9.41,$

$\theta = 4250.$

To calculate the thermodynamic properties of individual mixtures, the following components were used, which are presented in Table 3.

Table 3. Theoretical maximum density of reactant and enthalpy of formation values for ANFO components.

Component	H_f , kJ/mol	TMD, kg/m ³
Fuel oil (FO)	−29	830
Ammonium Nitrate (AN)	−365	1720
Polyethylene (PE)	−440	940
Polystyrene (PS)	53	1120
Polyvinyl chloride (PVC)	−83	1400
Polyurethane (PU)	−269	1050
Polypropylen (PP)	35	950

where: TMD—Theoretical maximum density of reactant (kg/m³), H_f —Enthalpy of formation at 298 K.

2.4. Methodology of Thermodynamic Calculations

Thermodynamic analyses were carried out for five basic plastics: polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyurethane (PU), which were additives to the ANFO-type explosives with the composition of 94.0% ammonium nitrate and 6.0% fuel oil. New recipe compositions of explosives containing the above-mentioned polymers were designed. In order to select the individual components of the mixture, a criterion close to zero oxygen balance with the highest possible content of plastics was adopted. The data of basic ANFO components and polymers contained in the database of the EXPLO5 computer program were used for the calculations. Due to the use of a small amount of plastics by weight, which are characterized by a density similar to the basic ANFO components, a density of 690 kg/m³ was assumed for all explosives. Thermodynamic calculations were performed to assess the impact of the use of individual plastics on ANFO performance. The assumption was to obtain the same or slightly different values of the determined parameters in relation to the reference ANFO. The composition of individual explosives and the adopted designations are presented in Table 4.

Table 4. Percentage content of individual Ex components and designations used.

Ingredients	Percentage of Ingredients								
Ammonium nitrate	94.00	94.00	94.00	94.00	94.00	94.00	94.00	94.00	94.00
Fuel oil	6.00	5.00	4.00	5.00	4.00	4.00	5.00	5.00	4.50
Polyethylene (PE)		1.00	2.00						
Polypropylene (PP)				1.00	2.00				
Polystyrene (PS)						2.00			
Polyvinyl chloride (PVC)							1.00		
Polyurethane (PU)								1.00	1.50
Ex name	ANFO	PE 1.0	PE 2.0	PP 1.0	PP 2.0	PS 2.0	PVC 1.0	PU 1.0	PU 1.5

3. Results

The results of individual calculations of the main thermodynamic parameters: explosion pressure, explosion temperature, explosion heat in constant volume, detonation velocity and volume of gases in constant volume, as well as oxygen balance, are presented in Table 5.

Table 5. List of calculated thermodynamic parameters.

Parameter	ANFO	PE 1.0	PE 2.0	PP 1.0	PP 2.0	PS 2.0	PVC 1.0	PU 1.0	PU 1.5
Explosion pressure (MPa)	3900	3807	3834	3824	3837	3808	3741	3879	3835
Explosion temperature (K)	2968	2946	2939	2961	2964	2969	2909	2957	2928
Explosion heat at constant volume (kJ/kg)	3914	3875	3860	3902	3914	3886	3761	3834	3758
Detonation velocity (m/s)	4410	4369	4370	4377	4384	4355	4312	4370	4356
Gas volume in standard conditions (l/kg)	1057	1059	1061	1059	1061	1049	1049	1052	1052
Oxygen balance (%)	−0.994	−1.12	−1.24	−1.12	−1.24	−0.54	1.03	0.05	0.57

In order to illustrate changes in individual parameters for explosives containing selected plastics, the percentage value of the parameter difference with respect to the reference ANFO was calculated (Table 6).

Table 6. Percentage difference in the values of the calculated parameters for explosives containing plastics.

Parameter	PE 1.0	PE 2.0	PP 1.0	PP 2.0	PS 2.0	PVC 1.0	PU 1.0	PU 1.5
Explosion pressure (MPa)	−2.38	−1.70	−1.95	−1.62	−2.37	−4.08	−0.54	−1.67
Explosion temperature (K)	−0.75	−0.97	−0.25	−0.13	0.03	−2.00	−0.36	−1.35
Explosion heat at constant volume (kJ/kg)	−0.99	−1.37	−0.31	0.00	−0.71	−3.91	−2.05	−3.99
Detonation velocity (m/s)	−0.92	−0.91	−0.75	−0.59	−1.25	−2.22	−0.91	−1.23
Gas volume in standard conditions (l/kg)	0.19	0.41	0.20	0.41	−0.75	−0.79	−0.44	−0.49

The results of the qualitative and quantitative analysis of post-detonation gaseous products are shown in Table 7.

Table 7. Changes in the composition of ANFO type gaseous explosive products with the chemical composition modified with plastics.

Product Name	The Name of the Explosive/Amount—Moles/kg								
	ANFO	PE 1.0	PE 2.0	PP 1.0	PP 2.0	PS 2.0	PVC 1.0	PU 1.0	PU 1.5
H ₂ O—Water	2.68×10^1	2.69×10^1	2.70×10^1	2.69×10^1	2.70×10^1	2.65×10^1	2.66×10^1	2.69×10^1	2.69×10^1
N ₂ —Nitrogen	1.17×10^1	1.17×10^1	1.17×10^1	1.17×10^1	1.17×10^1	1.17×10^1	1.16×10^1	1.17×10^1	1.17×10^1
CO ₂ —Carbon dioxide	3.96×10^0	3.90×10^0	3.84×10^0	3.90×10^0	3.83×10^0	4.17×10^0	3.92×10^0	4.05×10^0	4.01×10^0
CO—Carbon monoxide	4.24×10^{-1}	4.63×10^{-1}	5.03×10^{-1}	4.66×10^{-1}	5.08×10^{-1}	2.89×10^{-1}	5.92×10^{-2}	1.35×10^{-1}	7.88×10^{-2}
H ₂ —Hydrogen	2.37×10^{-1}	2.64×10^{-1}	2.92×10^{-1}	2.64×10^{-1}	2.93×10^{-1}	1.51×10^{-1}	3.37×10^{-2}	7.34×10^{-2}	4.39×10^{-2}
NO—Nitrogen(II) oxide	4.13×10^{-2}	3.55×10^{-2}	3.11×10^{-2}	3.79×10^{-2}	3.49×10^{-2}	6.78×10^{-2}	2.31×10^{-1}	8.69×10^{-2}	1.28×10^{-1}
OH—Hydroxide ion	1.33×10^{-2}	1.21×10^{-2}	1.11×10^{-2}	1.28×10^{-2}	1.23×10^{-2}	1.73×10^{-2}	2.91×10^{-2}	2.42×10^{-2}	2.85×10^{-2}
CH ₂ O ₂ —Formic acid	1.31×10^{-2}	1.43×10^{-2}	1.58×10^{-2}	1.45×10^{-2}	1.58×10^{-2}	8.89×10^{-3}	1.80×10^{-3}	4.08×10^{-3}	2.33×10^{-3}
O ₂ —Oxygen	6.70×10^{-3}	5.06×10^{-3}	3.92×10^{-3}	5.56×10^{-3}	4.66×10^{-3}	1.75×10^{-2}	2.37×10^{-1}	7.04×10^{-2}	1.65×10^{-1}
NH ₃ —Amonia	4.95×10^{-3}	5.85×10^{-3}	6.90×10^{-3}	5.83×10^{-3}	6.80×10^{-3}	2.52×10^{-3}	2.71×10^{-4}	9.51×10^{-4}	4.37×10^{-4}
H—Hydrogen ion	1.39×10^{-3}	1.42×10^{-3}	1.45×10^{-3}	1.48×10^{-3}	1.58×10^{-3}	1.15×10^{-3}	4.51×10^{-4}	7.67×10^{-4}	5.47×10^{-4}
H ₂ O ₂ —Hydrogen peroxide	4.43×10^{-4}	3.79×10^{-4}	3.31×10^{-4}	4.07×10^{-4}	3.75×10^{-4}	7.28×10^{-4}	2.44×10^{-3}	1.51×10^{-3}	2.20×10^{-3}
N ₂ O—Nitric oxide (I)	2.86×10^{-4}	2.45×10^{-4}	2.15×10^{-4}	2.62×10^{-4}	2.42×10^{-4}	4.71×10^{-4}	1.58×10^{-3}	1.38×10^{-4}	2.04×10^{-4}
O—Oxygen ion	2.74×10^{-4}	2.30×10^{-4}	1.97×10^{-4}	2.53×10^{-4}	2.35×10^{-4}	4.60×10^{-4}	1.38×10^{-3}	8.94×10^{-4}	1.24×10^{-3}
NO ₂ —Nitric oxide (IV)	1.43×10^{-4}	1.07×10^{-4}	8.36×10^{-5}	1.19×10^{-4}	1.00×10^{-4}	3.76×10^{-4}	4.91×10^{-3}	8.42×10^{-4}	1.93×10^{-3}
HNO—Nitoxyl (azanone)	3.55×10^{-5}	3.19×10^{-5}	3.35×10^{-5}	3.43×10^{-5}	3.31×10^{-5}	4.73×10^{-5}	7.42×10^{-5}	6.54×10^{-5}	7.44×10^{-5}
HCN—Hydrogen cyanide	2.06×10^{-5}	2.63×10^{-5}	2.90×10^{-5}	2.67×10^{-5}	3.39×10^{-5}	7.31×10^{-6}	1.53×10^{-7}	1.13×10^{-6}	2.96×10^{-7}
HCNO—Fulminic acid	1.91×10^{-5}	2.17×10^{-5}	2.44×10^{-5}	2.21×10^{-5}	2.52×10^{-5}	1.07×10^{-5}	9.79×10^{-7}	3.43×10^{-6}	1.52×10^{-6}
N—Nitrogen ion	1.21×10^{-6}	1.13×10^{-6}	1.08×10^{-6}	1.24×10^{-6}	1.28×10^{-6}	1.31×10^{-6}	8.77×10^{-7}	1.21×10^{-6}	9.99×10^{-7}
CNO—Fulminate ion	6.36×10^{-7}	6.65×10^{-7}	7.04×10^{-7}	7.12×10^{-7}	7.86×10^{-7}	4.60×10^{-7}	7.30×10^{-8}	2.05×10^{-7}	1.06×10^{-7}
CH ₃ OH—Methanol	2.93×10^{-7}	3.99×10^{-7}	5.40×10^{-7}	4.00×10^{-7}	5.33×10^{-7}	8.18×10^{-8}	8.61×10^{-10}	9.31×10^{-9}	1.93×10^{-9}
HCl—Hydrogen chloride							1.58×10^{-1}		
Cl—Chlorine ion							2.28×10^{-3}		
ClO = Chlorine monoxide							8.16×10^{-5}		
Cl ₂ —Chlorine							5.11×10^{-6}		

Table 7. Cont.

Product Name	ANFO	The Name of the Explosive/Amount—Moles/kg						PVC 1.0	PU 1.0	PU 1.5
		PE 1.0	PE 2.0	PP 1.0	PP 2.0	PS 2.0				
CClO—Carbon monoxidechloride							6.30×10^{-7}			
ClO ₂ —Chlorine(IV) oxide							3.33×10^{-8}			
Cl ₂ O—Chlorine(I) oxide							3.24×10^{-10}			
CH ₃ Cl—Chloromethane							9.47×10^{-13}			
CHCl ₃ —Chloroform							2.94×10^{-16}			

4. Discussion

Oxygen balances of individual explosives range from -1.24% to 1.03% , which is consistent with the principle of designing new compositions of explosives for civil purposes. The addition of plastics causes a percentage change in the value of thermodynamic parameters relative to ANFO in the range of -4.08% to 0.41% . Calculated for:

- explosion pressure, variability in the range -4.08% to -0.54% (range: 3.54),
- explosion temperature, variability in the range -2.00% to 0.03% (range: 1.97),
- heat of explosion, variability in the range -3.91% to 0.00% (range: 3.91),
- detonation velocities, variability in the range -2.22% to -0.59 (range 1.63),
- volume of gaseous products, variability in the range -0.79% to 0.41% (range: 1.20).

In the case of explosives containing individual plastics, for:

- PE 1.0: variability in the range -2.38% to 0.19% (range: 2.57),
- PE 2.0, variability in the range -1.70% to 0.41% (range: 2.11),
- PP 1.0, variability in the range -1.95% to 0.20% (range: 2.15),
- PS 2.0 variability in the range of -2.37% to 0.03 (range: 2.39),
- PVC 1.0, variability in the range -4.08% to -0.79% (range: 3.29),
- PU 1.0, variability in the range -2.05% to -0.36% (range: 1.69),
- PU 1.5, variability in the range -3.99% to -0.49% (range: 3.50).

The lowest values of the obtained parameters were recorded for PVC 1.0 (94% AN, 5% FO, 1% PVC) and PU 1.5 (94% AN, 4.5% FO, 1.5% PU). The most favorable values of thermodynamic parameters were found for PE 2.0 (94% AN, 4.5% FO, 1.5% PE), PP 1.0 (94% AN, 5% FO, 1% PP) and PU 1.0 (94% AN, 5% FO, 1% PU). With the exception of PU 1.5 and PVC 1.0, the differences in the estimated thermodynamic parameters in relation to ANFO are small, which allows us to assume that the operation of such an explosive will be similar in terms of energy to the reference one.

In the case of the designed explosives containing plastics, except for PVC 1.0, the qualitative structure of gaseous products resulting from detonation does not change. Due to the close to optimal (zero) oxygen balances, all the products formed are in the gaseous state. Plastics are chemical compounds of carbon and hydrogen, similar to the replaced oil; therefore, no new substrates are introduced into the structure of the explosive. Polyvinyl chloride, which is a branched chain polymer [CH₂CHCl], additionally introduces chlorine, which is responsible for the formation of such compounds as: HCl—hydrogen chloride, Cl—chlorine, ClO—chlorine oxide, Cl₂—chlorine, CClO—carbon monoxide chloride, ClO₂—chlorine(IV) oxide, Cl₂O—chlorine(I) oxide, CH₃Cl—chloromethane, CHCl₃—chloroform. In terms of the environment, these compounds are harmful to the environment and undesirable [36]. PVC 1.0 has the highest positive oxygen balance of all tested explosives $+1.03\%$, which causes an increased presence of nitrogen oxides NO₂ and N₂O and NO in relation to ANFO. The high chemical similarity of polyethylene (PE) and polypropylene (PP)—similar ratio of carbon

atoms to hydrogen, amounting to: C—33.33% to H—66.66% (ratio 0.33), which is similar to the fuel oil replaced by these components causes slight quantitative changes in individual gas products in relation to ANFO. PS 1.0 is characterized by a higher oxygen balance of -0.54% compared to explosives based on polyethylene and polypropylene. This causes an increase in the amount of nitrogen oxides NO_2 , N_2O and NO in relation to ANFO, a decrease in the amount of carbon monoxide CO and, consequently, free oxygen. Explosives containing the addition of polyurethane PU 1.0 and PU 1.5 have positive oxygen balances of $+0.05\%$ and $+0.57\%$, respectively. Polyurethane, which is a branched monomer $[\text{O-CO-NH}]$, introduces additional nitrogen into the explosive structure, which causes an increase in nitrogen oxides in the structure of post-detonation explosive products and free oxygen O_2 .

5. Conclusions

The conducted thermodynamic analyses allow the formulation of the following conclusions:

- In the case of modifying the chemical composition of the base ANFO, it is possible to obtain energy parameters comparable to saletrol (not lower than -2.05%). By replacing fuel oil in the amount of 1.0–2.0% (PE 2.0, PU 1.0 and PP 1.0) with these plastics, the adopted energy criterion is met (similar performance parameters to the basic ANFO).
- For the explosive PVC 1.0 containing polyvinyl chloride and an increased amount of polyurethane (PU 1.5), lower values of the estimated thermodynamic parameters are observed (up to 4.0%).
- Polymers have a similar chemical composition (polyvinyl chloride additionally contains chlorine, and polyurethane contains additional nitrogen), density and oxygen balance to the fuel oil. The addition of individual plastics (excluding PVC) does not change the quality of post-detonation products. The presence of products in a solid or liquid state of aggregation was not demonstrated in any case of the calculations, which is very advantageous. Small changes in the oxygen balance cause differences in the formation of the amount of moles of nitrogen oxides and carbon monoxide in relation to ANFO.
- Polyethylene and polypropylene show the greatest similarity of the parameters used by the EXPLO5 program algorithm (chemical formula, density and enthalpy of formation) to oil. As a result, explosives containing small amounts of these compounds (PE 1.0, PE 1.5 and PP 1.0, PP 2.0) have a similar composition of gaseous products in terms of both quantity and quality. Thus, the use of polyethylene and polypropylene instead of part of the fuel oil can be a way to dispose of these plastics, large amounts of which remain in landfills.
- The presence of chlorine in polyvinyl chloride causes a qualitative change in the composition of post-gas products formed as a result of the detonation of PVC 1.0. The simulations carried out indicate a significant, in terms of weight, amount of 9 chlorine compounds, which are particularly harmful to both the environment and humans.
- The simulations carried out do not take into account a number of factors that may have a potential impact on the actual values of the obtained energy parameters. Imperfect mixture explosives achieve variable values of performance parameters, depending on many factors. Performing “in situ” tests would allow for the verification of theoretical assumptions. Due to the use of small amounts of plastics, it is necessary to fragment them in order to uniformly introduce and homogenize them in the structure of the explosive for laboratory tests. Such a treatment is also possible to be used on an industrial scale by improving the technological process of ANFO production or adapting the existing mixing and loading devices to introduce an additional component in powder form.
- The limitation of thermodynamic simulation is also the difficulty in modeling polluting admixtures from waste materials. An important research issue is the impact of impurities (e.g., from bottle labels and organic residues) present in waste plastics lying in landfills on the effectiveness of the explosive.

- The production of explosives using waste plastics on an industrial scale may reduce the cost of producing the explosive. Due to the prevalence and significant amounts of plastic waste occurring all over the world, there is no threat of interrupting the supply chain (regardless of the energy crisis). In relation to oil, plastics are a low-cost component, the price of which is less dependent on the geopolitical situation in the world. The use of energy properties of plastics (especially those similar in structure to oil) for the production of explosives may have a pro-environmental aspect consisting of the recycling of waste. This approach is in line with the idea of recycling and the circular economy.
- According to data from 2020, approximately 24,900 tons of explosives are used annually in Poland for blasting works for civil purposes only in opencast mines [37]. Assuming the production of approximately 28% ANFO, out of this value containing 2.0% plastic, it is possible to reuse 139 tons of waste material per year.

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