

Article Thermodynamic Analysis of the Possibility of Using Biomass as a Component of High-Energy Materials

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Abstract: One of the unconventional, innovative ways of using biomass is using it as a component of high-energy material. According to conceptual assumptions, biomass can act as an energy carrier in modified high-energy materials-explosives (EX). Modification of the composition of the explosive requires the development of a method of introducing an additional component and changes its explosive and operational parameters (including safety). Thermodynamic calculation programs allow you to model the predicted energetic parameters of an explosive in order to select prospective compositions without the need to carry out a large number of costly and time-consuming field tests. This enables more effective design of new explosives compositions by narrowing down the scope of field tests using the "in situ" method. The use of renewable biomass as a corrector of EX properties may be a pro-environmental approach and reduces the production costs of the product. The thermodynamic simulations performed showed that, in the case of an appropriate proportion of ingredients, comparable and better energy properties were obtained in relation to the base composition. Moreover, the qualitative analysis of the sub-detonation products did not reveal the emission of additional gaseous components harmful to the environment compared to the reference explosive.

Keywords: biomass; high-energy materials; thermodynamic analysis

1. Introduction

Due to the development of urban planning and the increase in the global population, huge amounts of waste are generated, and consumption contributes to the production of biomass waste, which is a key social and environmental concern [1–3]. World production of plant biomass waste (generated as a result of agricultural and forestry activities) amounts to 140 Gt per year [4]. Proper management of such waste may contribute to minimizing the harmful impact on the environment in the case of landfilling (an element of waste management).

The guidelines for proper waste management are the waste hierarchy recommended by the European Waste Framework Directive [5,6]. The five main points of the Directive are ranked in the area of waste prevention and management:

- 1. avoidance/prevention;
- 2. re-use, through, among others, giving a new function;
- 3. recycling;
- 4. other recovery, incl. energy recovery (waste-to-energy WTE);
- 5. disposal.

In view of the adopted EU Directive [7] on the promotion of the use of energy from renewable sources, the WTE method from biomass seems to be the most justified. This direction of biomass use is promoted, among others, by the USA, Canada, China and



Citation: Biegańska, J.; Barański, K. Thermodynamic Analysis of the Possibility of Using Biomass as a Component of High-Energy Materials. *Energies* **2022**, *15*, 5624. https://doi.org/10.3390/en15155624

Academic Editor: F. Pacheco Torgal

Received: 14 July 2022 Accepted: 29 July 2022 Published: 3 August 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Poland [8]. Agricultural biomass is primarily used for the production of biofuels. It is estimated that by 2050, energy from biomass will cover more than 50% of energy needs in most developed countries [9]. Poland plans to generate at least 80% of its total energy from renewable sources, including biomass. More than 75% of biomass energy is to be produced from agricultural biomass [10]. The potential of agricultural biomass as an energy source has been the subject of research, among others, in India, China, Denmark, Poland and Nigeria [11–15]. The conversion into energy can take place either directly or indirectly. There are two main directions of using biomass for this purpose:

1. Biomass as a fuel;

The accumulated energy potential in biomass depends on the type of plant species and ranges from 16.3 to even 26.5 MJ/kg [16].

2. Biomass as a fuel in various forms;

Agricultural biomass can be used as an energy source in various forms, depending on its physical and chemical properties as well as availability:

directly as combustible fuel;

Worldwide, over 30% of household energy comes from agricultural biomass for heating and cooking [17].

as a gas fuel;

Biogas, produced from agricultural biomass, is stored and transported for domestic use to meet energy needs for heating, cooking and lighting. It is estimated that about 1.5 billion m³ of biogas can be produced from biomass using gasification processes [18].

• as liquid fuel;

Agricultural biomass can be used to produce ethanol [19]. Poland is a leading country that is taking steps to use agricultural ethanol additives in gasoline.

as granular fuel (fuel pellets);

The fuel pellets market in Poland is significantly expanding, and according to reports, over 720 Mg of pellets made of biomass are produced annually [20–28].

to generate electricity.

Producing electricity from biomass is a viable option in developing countries [29]. The use of biomass for electricity generation has also been reported in Europe and North America. In a study conducted in Poland in 2010 by the Ministry of Economy, it was found that the structure of biomass use will change within 20–25 years. Most of the biomass will be used to produce electricity and biofuels instead of producing heat [17]. Biomass conversion mainly takes place through combustion, gasification, pyrolysis, fermentation and chemical processes called transesterification [30]. The current use of biomass is invested as a renewable energy source (mainly obtained as an energy raw material) - for combustion or biogas production. Undertaking research will enable the use of waste biomass as an energy source in explosives.

An ANFO explosive is a simple, two-component mixture most often containing 94.0% ammonium nitrate (V) and 6.0% oil. Numerous attempts were made to modify the base composition of ANFO with various additives, including aluminum, copper, zinc, magnesium, coal dust, TNT, dolomite and silica powders [31–36] in order to improve the performance properties of the explosive. The use of guar gum, CMC, petroleum jelly, calcium stearates, kaolinite and polyurea to improve water resistance is described in [37–40]. The possibility of using biomass as a component of an explosive has not been described in the literature so far. The effect of the addition of an organic substance (rice straw, corn cob, sugar cane bagasse) on the ANFO detonation velocity (VOD) was presented only in [41].

2. Materials and Methods

2.1. Characteristics of the ANFO Explosive

Explosives for civil purposes are commonly used in mining for rock mass loosening and for engineering purposes (demolition, demining). It is the cheapest way of obtaining rock and energy resources. Due to the relatively low cost of production, the simplicity of production and the high availability of the necessary ingredients, a popular EX is Ammonium Nitrate Fuel Oil, commonly called ANFO-two-component mixture of granulated ammonium nitrate with liquid fuel (e.g., mineral oils, kerosene, mazout). Ammonium nitrate, which is the main component of ANFO, is characterized by a positive oxygen balance of +20% (it is an oxidant), a low detonation temperature of about 1500 $^{\circ}$ C, and a detonation speed of 1500–2300 m/s. It is hygroscopic and, therefore, lacks water resistance, which is a disadvantage of this component. The chemical form of the nitrate used in the production of ANFOs is of great importance. Granulated microporous nitrate has the best properties because, due to its high sorption capacity, it permanently bonds with the oil, thanks to which, due to the good mixing of ANFO ingredients, it obtains optimal blasting parameters. The oil is a combustible component of the mixture, increasing the specific heat of the EX: it has a low oxygen balance of about -300%, therefore it cannot be added in large amounts. ANFO explosives can be produced in bulk and sold in bags used for manual loading, but most often they are produced by mixing and loading systems at the point of consumption. The currently used structures of production and loading systems have an open structure, thanks to which they are relatively easy to expand with additional chambers. It is possible to mechanize the production process of the modernized ANFO type EX. Despite some disadvantages, ANFOs are often used in mining for blasting works. The currently observed trend shows that, despite the fact that ANFOs may seem already technologically obsolete, they are still an important group of explosives, therefore attempts to modify their chemical composition or refining with additives seem justified and prospective [42].

2.2. IT Tool—Computer Program for Thermodynamic Calculations

The ZMWCyw computer program developed by the Military University of Technology in Warsaw (Poland) was used to perform thermodynamic calculations. This program performs thermodynamic calculations in the variant of constant volume. The calculation algorithm is based on the European standard PN-EN 13631-15 [43]. The ZMWCyw program uses the method of minimizing the chemical potential described in the works [44–46]. The program allows you to calculate the most important thermodynamic parameters of explosives, such as explosion pressure, explosion temperature, heat of explosion in a constant volume, explosion force and gas volume under standard conditions. These parameters are the basic information about EX properties. The ZMWCyw program makes it possible to determine the qualitative and quantitative composition of the resulting subdetonation products and the form of their aggregation (state: gas, solid or liquid).

2.3. Description of the Methodology of Calculating Thermodynamic Parameters

The ANFO explosive with the composition of 94% ammonium nitrate (V) and 6.0% diesel oil was selected as the base - reference EX for modifying the composition (replacing its components). The data of the basic ANFO components needed to perform thermodynamic calculations were used from the database of the ZMWCyw program. The parameters needed to perform the calculations for biomass with a simplified chemical formula were adopted on the basis of research results [47]. The oxygen balance of individual explosives compositions was calculated using a spreadsheet using the algorithm described in the BN-80/6091-42 standard [48]. Thermodynamic simulations were performed by changing the formulation composition of the base ANFO according to four calculation variants, each time using a constant step of changing the proportion of components:

- variant 1.1—modification of the ANFO composition, replacing diesel oil with biomass;
- variant 1.2—modification of ANFO composition, replacing ammonium nitrate (V) with biomass;

- variant 1.3—modification of the ANFO composition, simultaneous replacement of ammonium nitrate (V) and diesel oil with biomass;
- variant 1.4—searching for the optimal proportions of ingredients (oxygen balance close to zero) of the composition at a constant biomass content of, respectively, 7.0%, 9.0%, 11.0% and 13.0%.

For the purposes of the calculations, the minimum step of the percentage change of the content of components of 0.5% by weight was adopted. In this way, the thermodynamic parameters (explosion temperature, explosion pressure, explosion heat, volume of explosion products, and explosion force) were calculated for 16 explosives' compositions and the base ANFO. Each explosive has been assigned the abbreviated designations given in Sections 3.1 and 3.2. The calculations performed under variants 1.1–1.3 allowed the gradual impact of the change in the base composition of the ANFO explosive on the value of the projected energy parameters to be determined. The simulations made according to the assumptions for variant 1.4 made it possible to determine the influence of the determined biomass content on the EX activities while maintaining an oxygen balance close to the optimal ones.

3. Results and Discussion

3.1. The Results of Thermodynamic Calculations of Variants 1.1–1.3 and Their Discussion

The basic thermodynamic parameter influencing the action of an explosive is the oxygen balance. It is considered that in the case of explosives consisting of several components (the so-called mixed EX), optimal energy parameters are obtained when the oxygen balance is close to zero. Excess or deficiency of oxygen in the structure of the explosive causes the formation of poisonous or environmentally harmful gas sub-detonation products [49]. The use of an additional component changes the chemical and functional properties of the mixture. The density also changes, which also affects the energy parameters of the modified explosives. A summary of changes in the value of the oxygen balance and density for individual EXs is presented in Tables 1–3.

Ingredients	Density [g/cm ³]	Oxygen Balance [%]			Percenta	ge of Ingred	ients		
Ammonium Nitrate (V)	0.82	20.00	94.00	94.00	94.00	94.00	94.00	94.00	94.00
Diesel	0.84	-348.25	6.00	5.50	5.00	4.50	4.00	3.50	3.00
Biomass	0.82	-139.05	0.00	0.50	1.00	1.50	2.00	2.50	3.00
	EX der	nsity	0.821	0.821	0.821	0.821	0.821	0.821	0.821
	EX oxygen	balance	-2.095	-1.049	-0.003	1.043	2.089	3.135	4.181
	EX na	me	ANFO	1.1/ B0.5	1.1/B1.0	1.1/B1.5	1.1/B2.0	1.1/B2.5	1.1/B3.0

Table 2. Oxygen balance and EX density of ANFO type with addition of biomass for variant 1.2.

Ingredients	Density [g/cm ³]	Oxygen Balance [%]	Percentage of Ingredients						
Ammonium Nitrate (V)	0.82	20.00	94.00	93.50	93.00	92.50	92.00	91.50	91.00
Diesel	0.84	-348.25	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Biomass	0.82	-139.05	0.00	0.50	1.00	1.50	2.00	2.50	3.00
	EX den	sity	0.821	0.821	0.821	0.821	0.821	0.821	0.821
	EX oxygen	balance	-2.095	-2.890	-3.686	-4.481	-5.276	-6.071	-6.867
	EX na	me	ANFO	1.2/B0.5	1.2/B1.0	1.2/B1.5	1.2/B2.0	1.2/B2.5	1.2/B3.0

Ingredients	Density [g/cm ³]	Oxygen Balance [%]			Percenta	ge of Ingred	ients		
Ammonium Nitrate (V)	0.82	20.00	94.00	93.00	92.00	91.00	90.00	89.00	88.00
Diesel	0.84	-348.25	6.00	5.00	4.00	3.00	2.00	1.00	0.00
Biomass	0.82	-139.05	0.00	2.00	4.00	6.00	8.00	10.00	12.00
	EX den	sity	0.821	0.821	0.821	0.821	0.821	0.821	0.820
	EX oxygen	balance	-2.095	-2.890	-2.095	-1.594	-1.092	-0.591	-0.089
	EX na	me	ANFO	1.3/B2.0	1.3/B4.0	1.3/B6.0	1.3/B8.0	1.3/B10.0	1.3/B12.0

Table 3. Oxygen balance and EX density of ANFO type with addition of biomass for variant 1.3.

The oxygen balance of the base ANFO calculated in the ZMWCyw computer program is -2.095%. In the case of variants 1.1 and 1.3, an increase in the EX oxygen balance was observed, containing an additional component- biomass. Biomass with the chemical formula given in [47] has an oxygen balance equal to -139.05%, and it is higher than in the case of diesel -348.25%. Therefore, replacing a combustible component with biomass will increase the resultant oxygen balance of the explosive. The optimal oxygen balance for the variant 1.1 occurs when the biomass content is 1.0% (1.1/B1.0; oxygen balance: -0.003). Even replacement of ammonium nitrate (V) and diesel fuel with biomass (variant 1.3) allows for obtaining an oxygen balance of modified ANFO close to zero, with a higher component content of 8.0% (1.3/B8.0; oxygen balance: -0.089) and 10.0% (1.3/B10.0; oxygen balance: -0.591%). In the case of replacing the exclusion of the oxidant- ammonium nitrate (V) with biomass (variant 1.2), a decrease in the oxygen balance is observed. Due to the obtained negative values of this parameter, the remaining thermodynamic calculations for EX for this variant were omitted. All compositions are of similar density.

The maximum heating temperature of the shot gases by the heat generated during the detonation of the explosive is defined as the explosion temperature and it is a parameter related to the explosion heat. Temperature is a catalyst that accelerates chemical reactions. The list of explosion temperature changes for individual EXs is presented in Figure 1.



y = equation of the trendline function R^2 —the coefficient of the quality of the model fit

Figure 1. Explosion temperature changes for individual explosives.

For the calculations of variant 1.1, the maximum value of the explosion temperature was found for 1.1/B1.0, it amounts to 2693.80 [K] and is higher compared to the base

ANFO (2663.00 K). At higher biomass contents, the explosion temperature drops sharply, which correlates with the lowering of the oxygen balance of subsequent EXs. In variant 1.3, the explosion temperature increases up to the content of 6.0% of biomass. For 1.3/B6.0 it amounts to 2678.90 [K] and it starts to decrease rapidly when the content of this component increases to 12.0%.

The basic parameter that determines the ability of an EX to perform work is the heat of the explosion, i.e., the energy released during an EX chemical reaction. The higher the parameter value, the greater the EX's ability to do its job. By using the method of successive approximations, it is possible to determine the temperature for the gaseous products of the explosion. The list of explosion pressure changes for individual EXs is presented in Figure 2.



y = equation of the trendline function R^2 —the coefficient of the quality of the model fit

Figure 2. Changes in the explosion heat for individual explosives.

The highest value of the heat of explosion for the calculations of variant 1.1 was found for 1.1/B0.5 (3989.30 kJ/kg) and 1.1/B1.0 (3985.30 kJ/kg). The calculated values are higher than the base ANFO (3957.90 kJ/kg). When the biomass content exceeds 1.0% by weight, the value of this parameter decreases in a linear manner. In variant 1.3, the obtained values of the heat of explosion are lower than the base ANFO. With the content of 2.0% of biomass for 1.3/B2.0, the obtained value was close to the reference EX, amounting to 3946.90 [kJ/kg].

The power of an explosion is defined as the amount of energy produced during an explosive transformation of 1 kg EX. A higher value of the parameter increases the potential of the EX's ability to do its job. The list of changes in the explosive force for individual EXs is presented in Figure 3.

Replacing small amounts of diesel with biomass in variant 1.1 causes a slight increase in the explosion force for 1.1/B0.5-74.00 [kJ/kg]. With the content of 1.0% of biomass for 1.1/B1.0 the parameter assumes the value of 969.90 [kJ/kg], and then it decreases. In the case of calculations of variant 1.3, a decrease in the value of the explosive force for all explosives was observed.

The volume of gaseous products is the total amount of detonation gases produced as a result of the explosive transformation of the explosive. The greater amount of produced gases in a constant volume increases the pressure on the rock medium. The addition of biomass does not change the qualitative structure of the post-blast gases. The summary of changes in the volume of explosion products for individual EXs is presented in Figure 4.



y = equation of the trendline function R^2 —the coefficient of the quality of the model fit



Figure 3. Changes in the explosive power for individual explosives.

y = equation of the trendline function R²-the coefficient of the quality of the model fit

Figure 4. Changes in the volume of explosive products for individual explosives.

As a result of replacing the basic components of ANFO with biomass, the volume of gaseous products decreases with the increase of this component in both variants of calculations. In the case of variant 1.1, the value of 977.80 kJ/kg obtained for 1.1/B3.0 is 1.97% lower than ANFO (997.40 kJ/kg). For EX 1.3/B12.0 the value of 950.90 kJ/kg was calculated, which is a decrease of 4.66% in relation to ANFO.

The volume of gaseous products in a constant volume is directly related to the explosion pressure. The list of explosion pressure changes for individual EXs is presented in Figure 5.

The applied biomass reduces the explosion pressure of the explosive, which was confirmed by the results of calculations for both variants. The lowest values of the parameters were recorded for variant 1.1 for 1.1/B3.0–2511.21 [MPa]. However, for variant 1.3 for 1.3/B12.0–2571.49 [MPa].



y = equation of the trendline function R^2 -the coefficient of the quality of the model fit

Figure 5. Explosion pressure changes for individual explosives.

A summary of the percentage changes in the values of individual parameters calculated for variants 1.1 and 1.3 is presented in Tables 4 and 5.

Table 4. Percentage change in the value of individual parameters for EX from variant 1.1 compared to ANFO.

Parameter	Unit	1.1/B0.5	1.1/B1.0	1.1/B1.5	1.1/B2.0	1.1/B2.5	1.1/B3.0
Explosion temperature; K	%	0.91	1.16	-0.70	-2.78	-4.89	-7.02
Constant volume heat of explosion; kJ/kg	%	0.79	0.68	-2.27	-5.47	-8.69	-11.91
Explosive power; kJ/kg	%	0.12	-0.30	-2.30	-4.46	-6.64	-8.85
Gas volume at standard conditions; L/kg	%	-0.78	-1.43	-1.61	-1.73	-1.85	-1.97
Explosion pressure; MPa	%	-0.38	-1.21	-3.36	-5.62	-7.91	-10.21

Table 5. Percentage change in the values of individual parameters for EX from variant 1.3 compared to ANFO.

Parameter	Unit	1.3/B2.0	1.3/B4.0	1.3/B6.0	1.3/B8.0	1.3/B10.0	1.3/B12.0
Explosion temperature; K	%	0.21	0.42	0.60	0.49	-0.42	-1.58
Constant volume heat of explosion; kJ/kg	%	-0.28	-0.56	-0.88	-1.60	-3.36	-5.43
Explosive power; kJ/kg	%	-0.66	-1.34	-2.04	-2.96	-4.48	-6.16
Gas volume at standard conditions; L/kg	%	-0.87	-1.74	-2.62	-3.43	-4.07	-4.66
Explosion pressure; MPa	%	-1.01	-2.02	-3.07	-4.53	-6.23	-8.06

The most favorable distribution of energy parameters for the calculations of variant 1.1 was obtained for the content of 1.0% of biomass for 1.1/B1.0. In this case, the explosion temperature (by 1.16%) and the heat of the explosion (by 0.68%) were higher than in ANFO. Other energy parameters decreased (decrease by 0.30% to 1.43%). A similarly favorable distribution of energy parameters values was obtained for 1.1/B0.5, i.e., higher than ANFO explosion temperature, heat of explosion and explosion power (increase from 0.12–0.91%) and slightly lower volume of gaseous products and explosion pressure (decrease from 0.38% to 0.78%). The observed dependence is the effect of equalizing the EX oxygen balance

caused by a lower oxygen balance of biomass in relation to diesel fuel. For 1.1/B3.0, the lowest values of energy indices were obtained (decrease by 1.97 to 11.91%).

The energy parameters of the explosives of variant 1.3, except for the explosion temperature, are lower compared to the base ANFO. Nevertheless, the simultaneous replacement of ammonium nitrate (V) and diesel allows for the introduction of more biomass into the EX structure while maintaining acceptable values of energy parameters. For 1.3/B2.0, the explosion temperature is slightly higher compared to ANFO (increase by 0.21%) and the decrease in the values of other parameters is insignificant (from 0.28% to 1.01%). With the content of 6.0% of biomass (1.3/B6.0), the highest value of the explosion temperature was obtained (an increase by 0.60% compared to ANFO), and other indicators decrease in the range from about 1.0–3.0%. In the case of the 1.3/B12.0 explosive containing 12.0% of biomass, the thermodynamic simulation showed a decrease in parameters by 1.58 to 8.06%.

3.2. The Results of Thermodynamic Calculations of Variant 1.4 and Their Discussion

A summary of changes in the value of the oxygen balance and density for individual EXs analyzed under variant 1.4 is presented in Table 6.

Table 6. Oxygen balance and A	ANFO-type EX density	y with the addition of biomass f	for variant 1.4
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Ingredients	Density [g/cm ³]	Oxygen Balance [%]	Percentage of Ingredients							
Ammonium Nitrate (V)	0.82	20.00	94.0	87.0	88.5	89.50	90.50			
Diesel	0.84	-348.25	6.0	0.0	0.5	1.5	2.5			
Biomass	0.82	-139.05	0.0	13.0	11.0	9.0	7.0			
	EX density		0.821	0.820	0.820	0.820	0.821			
EX	X oxygen balan	ce	-2.095	-0.677	0.663	0.162	-0.340			
	EX name		ANFO	1.4/B13.0	1.4/B11.0	1.4/B9.0	1.4/B7.0			

Changes in thermodynamic parameters for the explosives analyzed in variant 1.4 are presented in Table 7.

Table	7. Summar	y of calcı	ulated ther	nodynamic	parameters f	or variant	1.4
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Parameter	Unit	ANFO	1.4/B13.0	1.4/B11.0	1.4/B9.0	1.4/B7.0
Explosion temperature	Κ	2663.00	2652.80	2636.70	2650.20	2679.60
Constant volume heat of explosion	kJ/kg	3957.90	3817.10	3784.40	3822.80	3913.40
Explosive power	kJ/kg	972.80	924.90	921.10	928.30	949.10
Gas volume at standard conditions	l/kg	997.40	952.00	953.80	956.30	967.00
Explosion pressure	MPa	2796.85	2614.20	2597.17	2628.56	2695.24

The presented results show that despite the maintenance of an optimal oxygen balance close to zero, explosives enriched with a larger amount of biomass (11–13%) achieve lower values of thermodynamic parameters compared to compositions containing 7 and 9% of the additive. In the case of 1.4/B9.0 and 1.4/B7.0, the temperature and heat of explosion similar to ANFO were obtained. The highest in terms of the explosive power (949.10 kJ/kg) the volume of sub-detonation gas products (967.00 L/kg) and the explosion pressure (2695.24 MPa) in relation to ANFO were recorded for the composition containing 7.0% biomass, i.e., 1.4/B7.0.

The summary of the percentage changes in the values of individual parameters calculated for variant 1.4 is presented in Table 8.

Parameter	Unit	1.4/B13.0	1.4/B11.0	1.4/B9.0	1.4/B7.0
Explosion temperature; K	%	-0.38	-0.99	0.10	0.62
Constant volume heat of explosion; kJ/kg	%	-3.56	-4.38	-2.40	-1.12
Explosive power; kJ/kg	%	-4.92	-5.31	-3.68	-2.44
Gas volume at standard conditions, L/kg	%	-4.55	-4.37	-3.77	-3.05
Explosion pressure; MPa	%	-6.53	-7.14	-5.34	-3.63

Table 8. Percentage change in the values of individual parameters for EX from variant 1.4 compared to ANFO.

For explosive 1.4/B7.0, the explosion temperature increased by 0.62%, and other thermodynamic parameters decreased by 1.12–3.63% compared to ANFO. In the case of 1.4/B9.0, when the content of biomass in the EX structure is 9.0% by weight, the explosion temperature was close to that achieved by the base ANFO; other energy ratios decreased by about 2.4–5.3%. The greatest decrease in the energy potential was recorded for 1.4/B13.0 by about 0.4–6.5% depending on the parameter. The introduction of larger amounts of biomass to the EX causes a significant reduction in the amount of diesel. Too little or no liquid phase may contribute to worse homogenization of individual components of the mixture and thus achieve lower energy parameters in the case of biomass content above 11.0% by weight. With the given composition, it is not possible to obtain a zero oxygen balance when the amount of the ingredient exceeds 13.0%.

4. Conclusions

The conducted thermodynamic analysis of the impact of modification of the chemical composition of ANFO with biomass allows the following conclusions:

- In the case of thermodynamic calculations of variant 1.1—replacing diesel with biomass, the most favorable energy parameters were found for the composition: 1.1/B0.5 (94.0% ammonium nitrate (V), 5.5% diesel, 0.5% biomass) and 1.1/B1.0 (94.0% ammonium nitrate (V) 5.0% diesel, 1.0% biomass);
- The calculations made for variant 1.3—simultaneous replacement of ammonium nitrate (V) and diesel fuel showed that for EX containing 2.0% of biomass, i.e., 1.3/B2.0 (93.0% ammonium nitrate (V), 5.0% diesel, 2.0% biomass), 4.0% biomass; i.e., 1.3/B4.0 (92.0% ammonium nitrate (V), 4.0% diesel, 4.0% biomass) and 6.0% biomass; 1.3/B6.0 (91.0% ammonium nitrate, 3.0% diesel, 6.0% biomass), a decrease in thermodynamic parameters (apart from the explosion temperature) is insignificant and ranges from about 1.0–3.0%;
- Modification of the ANFO composition at a constant fixed biomass content while maintaining the optimal oxygen balance (variant 1.4) confirmed that the most favorable thermodynamic parameters were obtained for 1.4/B7.0 (90.5% ammonium nitrate (V), 2.5% diesel, 7.0% biomass), whose predicted thermodynamic parameters are lower than the base ANFO by about 1.1–3.6%;
- Thermodynamic simulations made in the ZMWCyw program helped obtain estimated values of the energy parameters of explosives calculated on the basis of a mathematical algorithm. The program does not take into account, inter alia, the distribution of individual components in the mixture (degree of homogenization), their fragmentation, chemical form, functional EX form, diameter of the load or the method of charge initiation;
- Initial tests (theoretical calculations) based on the general formula of biomass confirmed its suitability for use as a component in EX. Further research requires the use of a specific type of biomass (plant or animal), determining the elemental composition and energy parameters of the samples, and developing a technology for its introduction and homogenization with other components of the explosive. Due to the promising results, "in situ" tests in field conditions are planned in order to verify the theoretical assumptions;

The production of EX on the basis of ANFO with the use of biomass can contribute to lowering the cost of producing the explosive. It is a widely available, renewable and a low-cost component, unlike diesel fuel, the price of which depends on the geopolitical situation in the world and taxation and is subject to significant fluctuations. Industrial scale production of ANFO from biomass can reuse large amounts of waste substances. The potential economic benefits appear to be of particular importance in local conditions in economically developing countries. The use of energy properties of biomass for the purposes of EX production may contribute to environmental benefits consisting of the reuse of waste, which is part of the broadly understood idea of recycling and the circular economy. In Poland, for the purposes of blasting works only in opencast mines, about 7 million kg of EX are used annually (according to data from 2020). Assuming the production of only 20% of ANFO, out of this value containing 1.0% of biomass in its composition, it is possible to reuse 14,000 kg of the waste substance per year.

Author Contributions: Conceptualization, K.B.; Methodology, J.B.; Writing—original draft, K.B. and J.B.; Writing—original draft preparation, K.B.; Writing—review & editing, J.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author (K.B.).

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Das, S.; Lee, S.H.; Kumar, P.; Kim, K.H.; Lee, S.S.; Bhattacharya, S.S. Solid waste management: Scope and the challenge of sustainability. *J. Clean. Prod.* 2019, 228, 658–678. [CrossRef]
- Zhang, J.; Qin, Q.; Li, G.; Tseng, C.H. Sustainable municipal waste management strategies through life cycle assessment method: A review. J. Environ. Manag. 2021, 287, 112238. [CrossRef]
- Chen, H.; Li, J.; Liu, J.; Li, T.; Xu, G.; Liu, W. Thermodynamic and economic evaluation of a novel waste-to-energy design incorporating anaerobic digestion and incineration. *Energy Convers. Manag.* 2022, 252, 115083. [CrossRef]
- Tripathi, N.; Hills, C.D.; Singh, R.S.; Atkinson, C.H.J. Biomass waste utilisation in low-carbon products: Harnessing a major potential resource. *Clim. Atmos. Sci.* 2019, 2, 1–10. [CrossRef]
- Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on Waste and Repealing Certain Directives. 2008. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32008L0098 (accessed on 3 June 2022).
- Directive (EU) 2018/851 of the European Parliament and of the Council of 30 May 2018 Amending Directive 2008/98/EC on Waste. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2018.150.01.0109.01.ENG (accessed on 3 June 2022).
- Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the Promotion of the Energy from Renewable Sources. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32018L2001 (accessed on 3 June 2022).
- 8. Saleem, M. Possibility of utilizing agriculture biomass as a renewable and sustainable future energy source. *Heliyon* **2022**, *8*, e08905. [CrossRef]
- 9. Demirbas, A. Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. *Energy Convers. Manag.* **2008**, *49*, 2106–2116. [CrossRef]
- Wyszyński, Z.; Michalska-Klimczak, B.; Pagowski, K.; Kamińska, S. Biomass as the main source of renewable energy in Poland. In Proceedings of the International Scientific Conference, Jelgava, Latvia, 24–25 May 2012; pp. 91–96. Available online: https://llufb. llu.lv/conference/Renewable_energy_energy_efficiency/Latvia_Univ_Agriculture_REEE_conference_2012-91-96.pdf (accessed on 3 June 2022).
- 11. Terhi, S.; Liimatainen, H. Turning Grain Crop Residues into High-Value Extraction Compounds. 2017. Available online: http://www.oulu.fi/university/node/45466 (accessed on 3 June 2022).
- 12. Liu, H.; Jiang, G.M.; Zhuang, H.Y.; Wang, K.J. Distribution, utilization structure and potential of biomass resources in rural China: With special references of crop residues. *Renew. Sustain. Energy Rev.* **2008**, *12*, 1402–1418. [CrossRef]

- 13. Mahmood, A.; Hussain, A.; Shahzad, A.N.; Honermeier, B. Biomass and biogas yielding potential of sorghum as affected by planting density, sowing time and cultivar. *Pakistan J. Bot.* **2015**, *47*, 2401–2408.
- 14. Bechis, S. Possible impact of pelletised crop residues use as a fuel for cooking in Niger. In *Renewing Local Planning to Face Climate Change in the Tropics, Green Energy and Technology;* Springer: Cham, Switzerland, 2017; pp. 311–322. Available online: https://link.springer.com/chapter/10.1007/978-3-319-59096-7_15 (accessed on 3 June 2022).
- Baum, R.; Wajszczuk, K.; Peplinski, B.; Wawrzynowicz, J. Potential for agricultural biomass production for Energy purposes in Poland: A review. *Contemp. Econ.* 2013, 7, 63–74. Available online: https://www.econstor.eu/bitstream/10419/105415/1/75575 1248.pdf (accessed on 3 June 2022). [CrossRef]
- 16. Zajemska, M.; Musiał, D. Energetyczne wykorzystanie biomasy z produkcji rolniczej w procesie współspalania, Problemy Inżynierii Rolniczej Energy use of biomass from agricultural production in co-combustion proces). *Probl. Agric. Eng.* 2013, 4, 107–118. Available online: http://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-34bc2a3e-84e0-473d-9c74-c8 475402b292/c/Zajemska.pdf (accessed on 3 June 2022).
- Ministerstwo Gospodarki. Krajowy Plan Działania w Zakresie Energii ze Źródeł Odnawialnych. Warszawa 2010. Available online: https://wfosigw.wroclaw.pl/files/download_pl/769_krajowy-plan-dzialania-w-zakresie-energii-ze-zrodel-odnawialnych. pdf (accessed on 3 June 2022).
- Ahmed, T.; Ahmad, B. Burning of crop residue and its potential for electricity generation. *Pakistan Dev. Rev.* 2014, 53, 275–293. Available online: http://thepdr.pk/pdr/index.php/pdr/article/download/2613/2613 (accessed on 3 June 2022). [CrossRef]
- 19. Champagne, P. Feasibility of producing bio-ethanol from waste residues: A Canadian perspective Feasibility of producing bio-ethanol from waste residues in Canada. *Resour. Conserv. Recycl.* **2007**, *50*, 211–230. [CrossRef]
- Niedziółka, I.; Szpryngiel, M.; Kachel-Jakubowska, M.; Kraszkiewicz, A.; Zawiślak, K.; Sobczak, P.; Nadulski, R. Assessment of the energetic and mechanical properties of pellets produced from agricultural biomass. *Renew. Energy* 2015, 76, 312–317. [CrossRef]
- Obidziński, S. Pelletization of biomass waste with potato pulp content. *Int. Agrophys.* 2014, 28, 85–91. Available online: http: //www.international-agrophysics.org/pdf-104053-35122?filename=Pelletization%20of%20biomass.pdf (accessed on 3 June 2022). [CrossRef]
- Obidziński, S.; Piekut, J.; Dec, D. The influence of potato pulp content on the properties of pellets from buckwheat hulls. *Renew.* Energy 2016, 87, 289–297. [CrossRef]
- 23. Stolarski, M.J.; Szczukowski, S.; Tworkowski, J.; Krzyżaniak, M.; Gulczyński, P.; Mleczek, M. Comparison of quality and production cost of briquettes made from agricultural and forest origin biomass. *Renew. Energy* **2013**, *57*, 20–26. [CrossRef]
- Kijo-Kleczkowska, A.; Środa, K.; Kosowska-Golachowska, M.; Musiał, T.; Wolski, K. Combustion of pelleted sewage sludge with reference to coal and biomass. *Fuel* 2016, 170, 141–160. [CrossRef]
- Kijo-Kleczkowska, A.; Środa, K.; Kosowska-Golachowska, M.; Musiał, T.; Wolski, K. Experimental research of sewage sludge with coal and biomass co-combustion, in pellet form. Waste Manag. 2016, 53, 165–181. [CrossRef]
- Ciesielczuk, T.; Karwaczyńska, U.; Sporek, M. The Possibility of Disposing of Spent Coffee Ground with Energy Recycling. *J. Ecol. Eng.* 2015, *16*, 133–138. Available online: https://bibliotekanauki.pl/api/full-texts/2020/12/10/6011bb51-6f8e-4c28-ac3a-75d5 0befe737.pdf (accessed on 3 June 2022). [CrossRef]
- Cichy, W.; Witczak, M.; Walkowiak, M. Fuel Properties of Woody Biomass from Pruning Operations in Fruit Orchards. *BioResources* 2017, 12, 6458–6470. Available online: https://www.researchgate.net/publication/319095329_Fuel_Properties_of_Woody_ Biomass_from_Pruning_Operations_in_Fruit_Orchards (accessed on 3 June 2022). [CrossRef]
- Smaga, M.; Wielgosiński, G.; Kochański, A.; Korczak, K. Biomass as a Major Component of Pellets. *Acta Innov.* 2018, 26, 81–92. Available online: https://www.proakademia.eu/gfx/baza_wiedzy/465/nr_26_81-92_2_2_2.pdf (accessed on 3 June 2022). [CrossRef]
- Reddy, B.V.; Ramesh, S.; Kumar, A.A.; Wani, S.P.; Ortiz, R.; Ceballos, H.; Sreedevi, T.K. Bio-fuel crops research for energy security and rural development in developing countries. *BioEnergy Res.* 2008, 1, 248–258. Available online: https://link.springer.com/ content/pdf/10.1007/s12155-008-9022-x.pdf (accessed on 3 June 2022). [CrossRef]
- 30. Noor, S.; Latif, A.; Jan, M.; Ishaq, M. Overview of biomass conversion technologies. Sci. Vis. 2011, 16, 119–126.
- 31. Biessikirski, A.; Ziąbka, M.; Dworzak, M.; Kuterasiński, Ł.; Twardosz, M. Effect of metal addition on ANFO's morphology and energy detonation. *Przem. Chem.* 2019, *98*, 928–931.
- Zygmunt, B. Detonation parameters of mixtures containing ammonium nitrate and Aluminum. *Cent. Eur. J. Energ. Mater.* 2009, *6*, 57–66. Available online: http://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-article-BAT1-0034-0024 (accessed on 22 July 2022).
- Buczkowski, D.; Zygmunt, B. Detonation properties of mixtures of ammo nium nitrate based fertilizers and fuels. *Cent. Eur. J. Energ. Mater.* 2011, *8*, 99–106. Available online: http://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-article-BAT1-0039-0032 (accessed on 22 July 2022).
- 34. Sitkiewicz-Wołodko, R.; Maranda, A.; Paszula, J.M. Modification of ANFO Detonation Parameters by Addition of Ground of Ammonium Nitrate(V) and Aluminium Powder. *Cent. Eur. J. Energ. Mater.* **2019**, *16*, 122–134. Available online: https://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-d2207b5e-2c74-49c3-a5b2-757b147f3315?q=bwmeta1.element.baztech-dae6be4c-5cfd-47bb-b1d9-c1bad932575b;8&qt=CHILDREN-STATELESS (accessed on 22 July 2022). [CrossRef]

- Biessikirski, A.; Barański, K.; Pytlik, M.; Kuterasiński, Ł.; Biegańska, J.; Słowiński, K. Application of Silicon Dioxide as the Inert Component or Oxide Component Enhancer in ANFO. *Energies* 2021, 14, 2152. Available online: https://www.mdpi.com/1996-1 073/14/8/2152/pdf (accessed on 22 July 2022). [CrossRef]
- Miyake, A.; Kobayashi, H.; Echigoya, H.; Kubota, S.; Wada, Y.; Ogata, Y.; Arai, H.; Ogawa, T. Detonation characteristics of ammonium nitrate and activated carbon mixture. *J. Loss Prev. Process Ind.* 2007, 20, 584–588. [CrossRef]
- Sheeran, H.; Sheeran, J. Water Resistant Sensitizing Additive for Ammonium Nitrate Blasting Agents. U.S. Patent US4780156A, 25 October 1988. Available online: https://patents.google.com/patent/US4780156A/en (accessed on 22 July 2022).
- Sheeran, J. Water Blocking in Explosive Compositions. U.S. Patent CA02912246, 10 April 2013. Available online: https://patents. google.com/patent/CA2812246A1/en (accessed on 22 July 2022).
- 39. Damse, R. Waterproofing materials for ammonium nitrate. Def. Sci. J. 2004, 54, 483–492. [CrossRef]
- 40. Sugihara, H.; Noguchi, K.; Yoshihara, K.; Sato, Y. Development and field-blasting tests of water-resistant granular explosive. *Sci. Technol. Energ. Mater.* **2005**, *66*, 389–392.
- Resende, S.A.; Silva, V.C.; Lima, H.M. Study of non-conventional fuels for explosives mixes. *Rem Rev. Esc. Minas* 2014, 67, 297–302. [CrossRef]
- Biegańska, J.; Barański, K. Wpływ dodatków odpadowych tworzyw sztucznych na parametry energetyczne EX typu ANF (Effect of plastic waste additives on the energetic parameters of ANFO explosives). *Mater. Wysokoenergetyczne/High Energy Mater.* 2017, 9, 145–158. [CrossRef]
- PN-EN 13631-15 2007; Materiały wybuchowe do użytku cywilnego—Materiały wybuchowe kruszące—Cześć 15: Obliczanie właściwości termodynamicznych. In Explosives for Civil Uses—High. Explosives—Calculation of Thermodynamic Properties. Polish Committee for Standardization: Warsaw, Poland, 2007.
- 44. Grys, S.; Trzcinski, W.A. Termodynamiczne modelowanie procesów spalania, wybuchu i detonacji nieidealnych układów wysokoenergetycznych (Thermodynamic modeling of combustion, explosion and detonation processes of non-ideal high-energy systems). *Biuletyn WAT* 2010, 59. Available online: https://yadda.icm.edu.pl/yadda/element/bwmeta1.element.baztech-article-BWA9-0041-0050/c/httpwww_wat_edu_plm000000biuletyndownload_phptable3bazaartykulowfielddodajpobierzkey1220. pdf (accessed on 22 July 2022). (Only In Polish).
- 45. Mader, C.H. Numerical Modeling of Detonations; University of California, Berkley: Berkley, CA, USA, 1979.
- 46. White, W.B.; Johnson, S.M.; Danzig, G.B. Chemical equilibrium in complex mixtures. J. Chem. Phys. 1958, 28, 751–755. [CrossRef]
- Peduzzi, E.; Boissonnet, G.; Maréchal, F. Biomass modelling: Estimating thermodynamic properties from the elemental composition. *Fuel* 2016, 181, 207–217. [CrossRef]
- BN 80 6091 42; Górnicze Materiały Wybuchowe—Obliczanie parametrów użytkowych. In Mining Explosives—Calculation of Utilities Parameters. Polish Committee for Standardization: Warsaw, Poland, 1980.
- Sitkiewicz-Wołodko, R.; Maranda, A. Analiza wybranych parametrów saletroli i emulsyjnych materiałów wybuchowych (Analysis of selected parameters of saletrols and emulsion explosives). *Chemik* 2016, 70, 3–18. Available online: https://miesiecznikchemik.pl/wp-content/uploads/2016/03/1_16_Maranda_PL.pdf (accessed on 3 June 2022). (Only In Polish).