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Determination of environmental burden of combustion products of pyrotechnic mixtures to quarrying operations
Określenie obciążeń środowiskowych produktami spalania mieszanin pirotechnicznych stosowanych do urabiania złóż blocznych

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Abstract: *Using the ICT-Thermodynamic Code program, thermodynamic parameters and combustion products composition of the Rocksplitter type, containing different masses of pytotechnic mixture and black powder, were evaluated. The eco-indicator was determined on the basis of numerical falsification results obtained using the SimaPro PhD version 7.2 of the Dutch company PreConsultants. The environmental impact analysis was performed at the combustion temperatures of the tested mixtures and at 298 K.*
Streszczenie: *W ramach niniejszej pracy, stosując program ICT-Thermodynamic Code oszacowano parametry termodynamiczne i składy produktów spalania ładunków typu Rocksplitter zawierających różne masy mieszaniny pirotechnicznej i prochu czarnego. Na podstawie uzyskanych rezultatów falsyfikacji numerycznych, stosując program SimaPro PhD wersji 7.2 holenderskiej firmy PreConsultants, wyznaczono potencjalny wpływ na środowisko metodą Ekowskaźnik 99. Analiza obciążeń środowiska została wykonana dla temperatur spalania testowanych mieszanin oraz temperatury 298 K.*

Keywords: *Rocksplitter, black powder, combustion products, eco-indicator*
Słowa kluczowe: *Rocksplitter, proch czarny, produkty spalania, ekowskaźnik*

1. Introduction

Miners have been utilising the new blasting agent (gas generator), Rocksplitter, for several years. It is used for quarrying operations and in technical blasting [1-4]. As with black powder, it is an oxidant-flammable system. The result of the reaction of these components is generation of a large amount of thermal energy and gaseous combustion products causing a rapid pressure increase in the blasthole, which results in fragmentation of the block deposit. Concurrently, the generated combustion products may create pollution of the local environment. Therefore, this work involves a comparative environmental impact analysis of black powder used thus far and the Rocksplitter loads.

2. Materials and research methods

Thermodynamic parameters and composition of explosion products were determined for four types of blasting agents (gas generators) – Rocksplitters (Table 1). Individual gas generators contained 84-87.7% of sodium chlorate ($NaClO_3$) and 8.3-8.63% of oil and small masses of black powder, as well as about 1% of iron(III) oxide (Fe_2O_3) used in the ignition system.
Data were collected by estimations performed using the ICT-Thermodynamic Code tool [5], and data on the potential burden were taken from the Euroinvent database in the SimaPro 7.2 PhD software and modelled on the basis of the analysis endpoints. During the calculations in SimaPro 7.2 PhD, data obtained from the following libraries: Ecoinvent v.2, IDEMAT 2001 and BUWAL250, were also used. The third stage of the life cycle analysis was the **L**ife **C**ycle **I**mpact **A**ssessment *(*LCIA). The analyses were performed in the SimaPro 7.2 PhD software utilising the method used for assessing the impact of technology on the environment – *Eco-indicator 99*. The *Eco-indicator 99* method enabled the presentation of the technological impact on the environment using three indicators, according to the categories of impact: human health, ecosystem quality and resource consumption. The final result of the calculations is presented in the eco-indicator points, [Pt].

Table 1. Ingredients of the analysed Rocksplitters and black powder charges

Ingredient	Ingredients [%]				
	R 50	R 100	R 150	R 200	Black powder
$NaClO_3$	84.00	85.50	86.90	87.70	–
Fe_2O_3	1.00	1.00	1.00	1.05	–
Gas oil	8.30	8.40	8.60	8.63	–
KNO_3	5.02	3.82	2.62	1.96	75.00
Sulphur	0.67	0.51	0.35	0.26	10.00
Coal	1.03	0.77	0.53	0.38	15.00

3. Numerical estimation of combustion products

The calculation results are summarised in Table 2 and in Figs. 1-4 and are compared in Fig. 5 and 6.

Table 2. The results of calculations of the thermodynamic parameters of Rocksplitter charges

Rocksplitter	Oxygen balance [%]	Combustion pressure [bar]	Combustion temperature [K]	Volume of gas products [mol/kg]	E_s [J/g]	Heat of combustion [J/g]
R 50	8.67	535	2813	23.79	561	4491
R 100	9.34	531	2817	23.89	559	4446
R 150	9.62	533	2796	24.03	563	4445
R 200	10.06	528	2796	24.07	559	4409

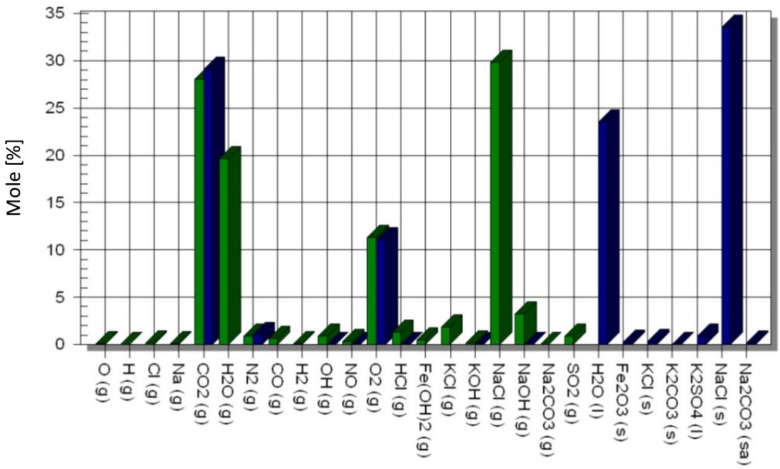


Figure 1. Reaction products for Rocksplitter 50 for a combustion temperature of 2813 K and a normal temperature of 298 K

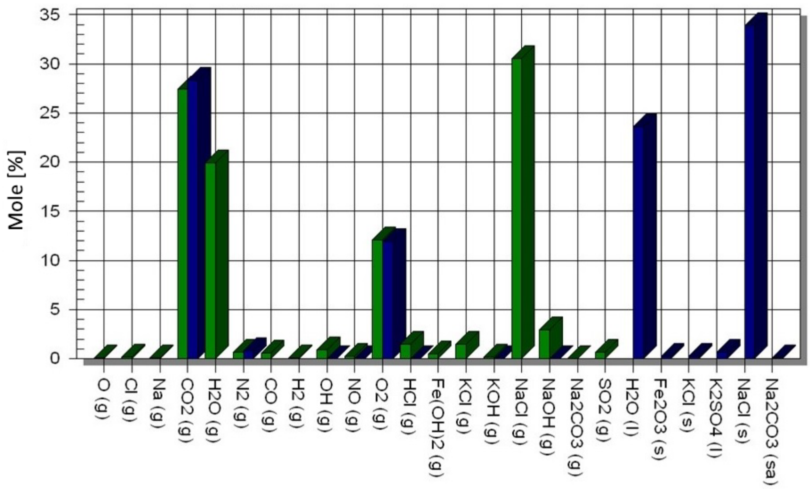


Figure 2. Reaction products for Rocksplitter 100 for a combustion temperature of 2817 K and a normal temperature of 298 K

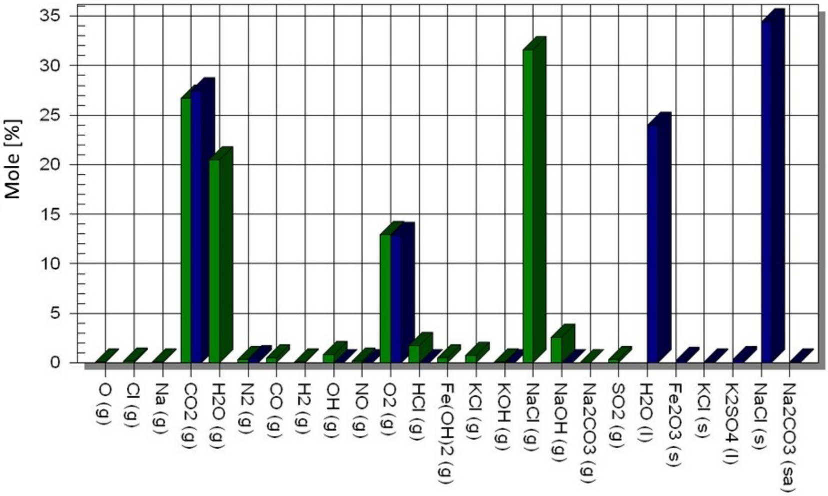
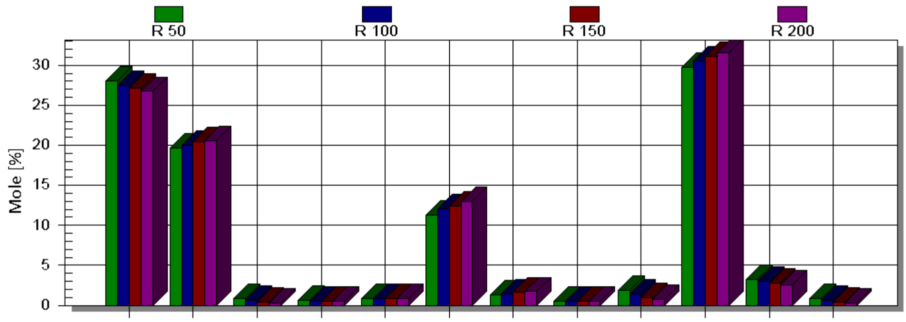


Figure 3. Reaction products for Rocksplitter 150 for a combustion temperature of 2796 K and a normal temperature of 298 K



	CO2 (g)	H2O (g)	N2 (g)	CO (g)	OH (g)	O2 (g)	HCl (g)	Fe(OH)2 (g)	KCl (g)	NaCl (g)	NaOH (g)	SO2 (g)
R 50	28.055	19.648	0.886	0.622	0.905	11.290	1.336	0.524	1.891	29.792	3.242	0.871
R 100	27.480	19.965	0.655	0.538	0.880	12.088	1.452	0.521	1.448	30.550	2.951	0.660
R 150	27.107	20.416	0.428	0.531	0.902	12.397	1.647	0.517	0.996	31.148	2.734	0.451
R 200	26.753	20.524	0.309	0.472	0.870	12.944	1.705	0.541	0.749	31.584	2.563	0.337

Figure 4. Reaction products for Rocksplitter 200 for a combustion temperature of 2796 K and a normal temperature of 298 K

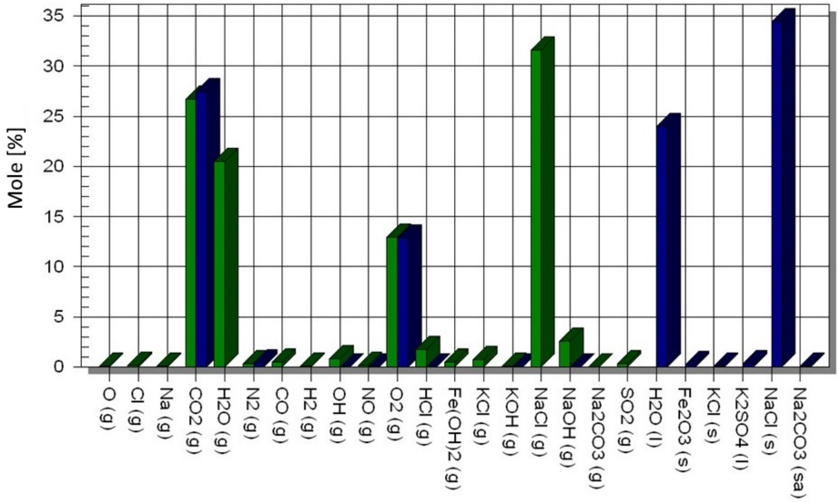
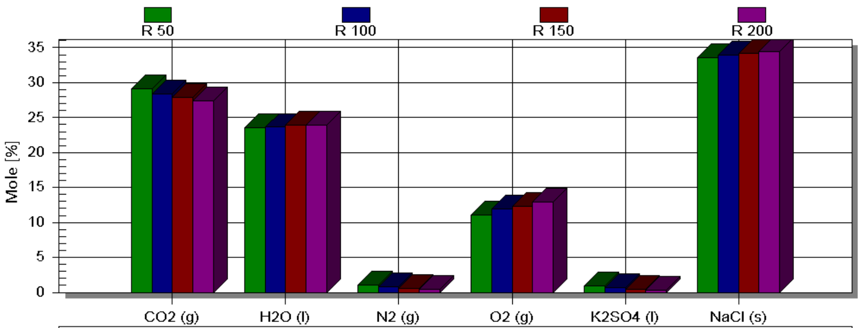


Figure 5. Comparison of the content of combustion products for individual Rocksplitters for the relevant combustion temperatures



	CO2 (g)	H2O (l)	N2 (g)	O2 (g)	K2SO4 (l)	NaCl (s)
R 50	29.126	23.541	1.061	11.042	0.897	33.562
R 100	28.371	23.621	0.800	11.936	0.677	33.919
R 150	27.921	23.970	0.543	12.308	0.460	34.246
R 200	27.454	23.954	0.404	12.889	0.343	34.459

Figure 6. Comparison of the content of combustion products for individual Rocksplitters at relevant combustion temperatures and at a normal temperature of 298 K

The thermodynamic parameters of the charges of individual types of Rocksplitters, differ by less than 5% when compared to CO_2 emissions. The higher the ratio between the active mass and the igniting mass (black powder), the lower the pressure and temperature of combustion and energy parameters, and the higher the volume of gaseous products of combustion. The main reaction products for the tested mixtures are:

- carbon dioxide,
- water (in gaseous or liquid form),
- dioxide and sodium chloride.

Additionally, low amounts of dinitrogen and potassium sulphate were estimated in the reaction products. Along with an increase in the Rocksplitter charge mass, a decrease in the carbon dioxide content is also observed, which is associated with a lower amount of black powder, for which the results of falsification of combustion products are illustrated in Fig. 7.

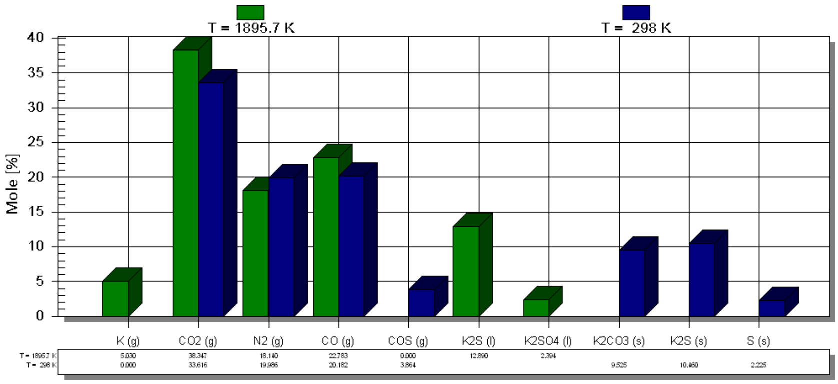


Figure 7. Estimated products of black powder combustion for the combustion temperature of 1895.7 K and normal temperature of 298 K

4. Analysis of the environmental loads

Combustion products may be the primary hazards generated during the combustion of the Rocksplitter mixtures. Therefore, this factor was taken into account during analysis of the environmental loads based on the **L**ife **C**ycle **A**ssessment (LCA) using the *Eco-indicator 99* method. In the *Eco-indicator 99* method, the environmental profile refers to 11 impact categories, which model the environmental impact at the endpoint stage of the environmental mechanism. All impact categories are assessed in relation to the three main harm categories, *i.e.* human health, ecological effects and resource consumption. Unit of the **D**isability **A**djusted **L**ife-**Y**ears characterisation parameter, [DALY], denotes years of life corrected by disability and is an indicator used to determine the state of health of a given society. Moreover, it expresses the total years of life lost as a result of premature death or damage to health following injury or illness. The unit of the characterisation parameter [PDF·m^2·year] – some species potentially endangered, refers to the damage shown as the disappearance of certain species in a given area and at a given time. The main harm and impact categories in the *Eco-indicator 99* method are presented in Table 3.

Table 3. List of major injury and impact categories in the *Eco-indicator 99* method [6]

Impact category	Unit of the characterisation parameter	Name of the impact category
Human health	[DALY]	Carcinogenity / Carcinogens
		Respiratory system (inorganic compounds) / Resp. inorganics
		Respiratory system (organic compounds) / Resp. organics
		Climate changes
		Radiation
		Ozone layer
Ecosystem quality	[PDF·m^2·year]	Ecotoxicity
		Acidification/Eutrophication
		Land management / Land use
Resource usage	[MJ]	Mineral resources / Minerals
		Fossil fuel resources / Fossil fuels

In the Eco-indicator method, the weighted values of indicators of environmental impact categories are calculated to determine the weight of individual environmental aspects and to approximate the possibilities of their comparison. Weighting usually leads to a much lower number of category indicators (in this case three), and even to one indicator value (total value of the indicator – Pt), which allows for easy comparisons to be made. This is done by setting the values of the weight multipliers for certain standardised environmental impact category indicators. In the Eco-indicator method, the results of the harm category indicators are normalised, weighted and grouped into the final eco-indicator, which means that the environmental impact assessments lead to the determination of the impact in the form of one number expressing the number of eco-indicator points. The current study uses one of several versions of computational procedures as a part of a magnitude assessment of the impact in the *Eco-indicator* method, the so-called cultural versions offered by the PreConsultants company Hierarchical (H), individualistic (I) and egalitarian (E) versions exist. Each of these versions may use the average weighting criteria (A) or weightings typical for a given version (H, E or I). The normalisation criteria used in the cultural versions provide information on the magnitude of the reference streams expressing the average annual impact on the European citizen, to which the normalisation stage refers. The weighting criteria provide information on the validity of the harm category. In the cultural I/A version, greater importance is given to the disorders connected to human health and the environment (weighting value 400) than to natural resources (weighting value 200). All cultural versions with average weighting criteria, *i.e.* E/A, I/A, H/A are characterised by this proportion. Conversely, the normalisation criteria are different. The H/A version was used in our work due averaging of the values. Table 4 presents the weighting and normalisation criteria used in the utilised cultural version in the *Eco-indicator 99* method.

Table 4. Weighting and normalisation criteria used in the Eco-indicator 99 method in cultural version H/A [6]

Criterion	Criterion of normalising	Criterion of weighting
Human health	1.141E2 [DALY]	400 [Pt]
Ecosystem quality	1.748E–4 [PDF·m^2]	
Resource usage	1.325E–4 [MJ]	200 [Pt]

The life cycle analysis was carried as a result of obtaining the source data from Sima Pro PhD version 7.2 software of the Dutch company PreConsultants. The analysis of environmental loads was carried out for the combustion temperatures of the tested pyrotechnic mixtures and for the normal temperature of 298 K. In the case of potential environmental dangers, the temperature of 298 K, to which the combustion products can potentially cool under operating conditions, is of primary importance. The calculations were carried out at the stage of combustion (usage) of the tested mixtures and at a normal temperature of 298 K for comparison. The results are summarised in Table 5.

Table 5. Eco-indicator values for Rocksplitter and black powder charges

Eco-indicator values [Pt]	R50	R100	R150	R200	Black powder
	Temperature of 298 K				
Human health	24564	24825	25064	25219	31738
Ecosystem quality	0	0	0	0	0
Resource usage	0	0	0	0	0
	Temperature of 2796 K				Temperature of 1896.7 K
Human health	150	116	83	64	24
Ecosystem quality	4	3	2	2	0
Resource usage	0	0	0	0	0

Based on Table 5, it is possible to identify which harm category for the combustion stage has a dominant impact. Specifically, which of the impact categories within a given harm category is relevant, as different values exist for the indicator of each impact category. Furthermore, based on Table 5, it can be concluded that the key parameter used for evaluating the degree of environmental impact for the combustion stage is the temperature used in the process. The eco-indicator value estimated for a normal temperature of 298 K is much higher for black powder than for Rocksplitters.

In Figs. 8 and 9 a comparison of the potential impact of the analysed materials at a normal temperature of 298 K on the damage category and the impact category for Rocksplitters and black powder is presented, respectively.

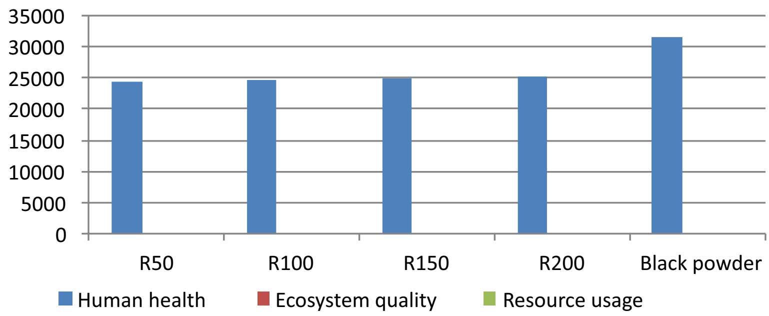


Figure 8. Eco-indicator values [Pt] of the analysed materials at a normal temperature of 298 K for individual damage categories in the *Eco-indicator 99* method

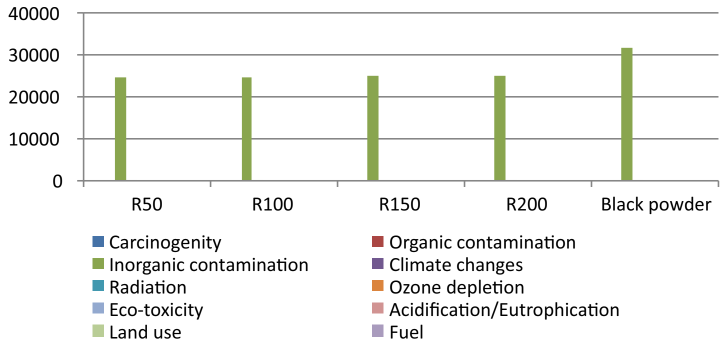


Figure 9. Eco-indicator values [Pt] of the analysed materials at a normal temperature of 298 K for the category of impact in the *Eco-indicator 99* method (only values for the "Inorganic contamination" category are visible, as they are significantly greater than 0)

Based on the data summarised in Figs. 8 and 9, it can be concluded that the main areas of impact are categories of damage to human health – contamination with inorganic compounds. The values of the impact category for this type of dust, assuming that it is in the range of 2.5 to 10 μm, *i.e.* in the range of the size of dust particles included in the Sima Pro PhD databases, is most important for this group of materials. The impact of carbon dioxide on the climate change is of marginal quantitative importance in this case.

In Fig. 10 and 11 a comparison of the potential impact of the analysed explosives at the combustion temperatures for Rocksplitter products and at 1896.7 K for black powder for the damage and the impact categories is shown, respectively.

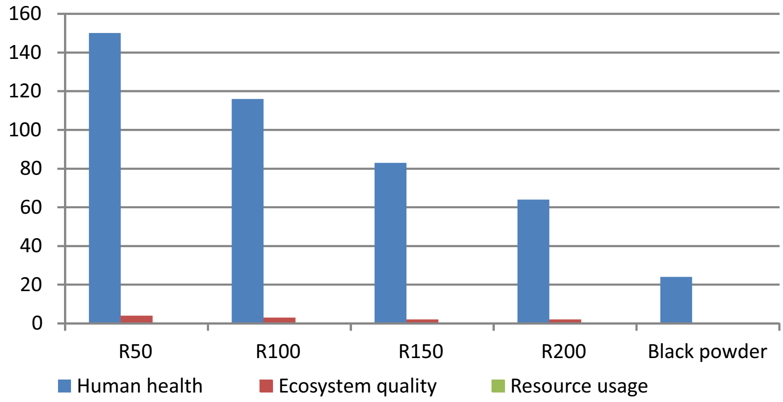


Figure 10. Eco-indicator values of the analysed materials at combustion temperatures for Rocksplitter products and at 1896.7 K for black powder for the damage category in the *Eco-indicator 99* method (the values for the "Resource use" category are not visible as they are in the order of 0)

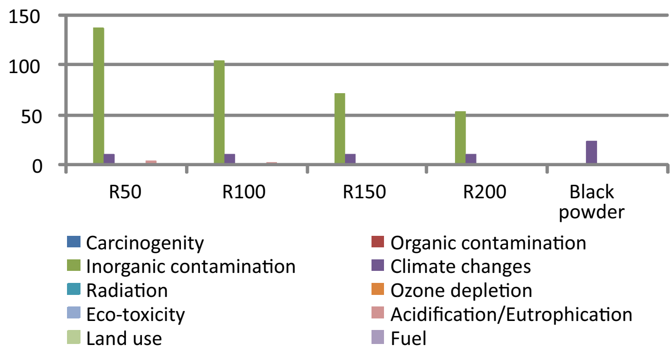


Figure 11. Eco-indicator values of the analysed materials at combustion temperatures for Rocksplitter products and at 1896.7 K for black powder for the impact category (values, which are not shown in the figure are in the order of 0)

Data shown in Figs. 10 and 11 indicate that the main impact areas are the categories of damage to human health and the quality of the ecosystem, and within these categories of damage the most important are impact categories, *i.e.* contamination with inorganic compounds, climate changes as well as acidification and eutrophication.

5. Summary

The analysis of environmental loads was carried out for the combustion temperatures of the pyrotechnic mixtures tested and the normal temperature of 298 K. In the case of potential environmental hazards, the temperature of 298 K, which the combustion products can potentially cool to under operating conditions, is of most importance. In this case, higher values of *Eco-indicator 99* were obtained for black powder (31738 Pt, respectively). The calculations were carried out exclusively for the combustion stage (usage) of the tested mixtures and the normal temperature.

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