# RESEARCH OF THERMODYNAMIC CHARACTERISTICS OF A GAS-GENERATING COMPOSITION BASED ON AMMONIUM PERCHLORATE

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Larissa R. Sassykova
Al-Farabi Kazakh National University


s.Kh. Aknazarov
ТОО НПТЦ "Жалын"


Marat I. Tulepov
Al-Farabi Kazakh National University

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# RESEARCH OF THERMODYNAMIC CHARACTERISTICS OF A GAS-GENERATING COMPOSITION BASED ON AMMONIUM PERCHLORATE

Zh. A. Amir, Zh. B. Kudyarova, D. A. Baiseitov, L. R. Sassykova and O. Y. Golovchenko
S. Kh. Aknazarov, M. I. Tulepov, A. Ye. Orazbayev and Sh. E. Gabdrashova
Al-Farabi Kazakh National University, Almaty, Kazakhstan
E-Mail: larissa.rav@mail.ru

## ABSTRACT

The thermodynamic characteristics of combustion processes of a gas-generating composition based on ammonium perchlorate have been investigated. Polyethylene was chosen as a fuel, the choice in favor of this component is due to the fact that ammonium perchlorate readily interacts with polyethylene, and this fuel contributes to the rapid decomposition of ammonium perchlorate. The optimal composition of the mixture was found. It has been established that the highest efficiency and specific gas production are observed in the area of stoichiometric ratio of the initial components of gas generator compositions. The influence of the oxidizing agent ammonium perchlorate on the energy release of composite energetic materials, the thermal decomposition of ammonium perchlorate and ammonium perchlorate with polyethylene was studied by thermogravimetry and differential scanning calorimetry. In research for simultaneous thermal analysis of the ammonium perchlorate samples and the mixture of ammonium perchlorate with polyethylene (the portion of mixture was 8.6 mg, pure ammonium perchlorate was 10 mg, and the heating rate was 10°C / min.) was found that at temperatures around 514 K, an endothermic peak is observed corresponding to a polymorphic transition in the crystal structure of ammonium perchlorate, in both cases the peaks coincide. At a temperature of about 645.3 K, an exothermic peak can be observed, at which the oxidation of polyethylene occurs with a large release of energy. The peak at 702.2 K corresponds to the decomposition of ammonium perchlorate. The developed gas generator composition based on ammonium perchlorate can be used for open pit mining for splitting block stone in a gentle mode or breaking hard mineral rocks. This composition is safe from an environmental point of view, there are no toxic gases such as carbon monoxide and nitrogen oxides in the products.

**Keywords:** gas generator, ammonium perchlorate, polyethylene, synchronous thermal analysis, thermodynamic characteristics.

## INTRODUCTION

In the development of gas-generating compositions and products based on them, nitrates and perchlorates are widely used. They have a low cost, favorable operational and technological characteristics. Basically, interest in the development of compositions based on nitrates and perchlorates is due to the possibility of utilizing household waste, namely, using polyethylene (PE) or polyethylene terephthalate (PET) as combustible. Therefore, the search for new, available components of gas-generating compositions with a wide raw material base is a topical research.

Research and development of energy compositions based on ammonium perchlorate is an important task in the field of creating high-energy materials. Compositions of this type are distinguished by low sensitivity to various influences, environmental friendliness of combustion products and low cost [1].

As shown in the literature [2], the amount of polymer material that accelerates the combustion of perchlorates is in the range from 4.0 to 21.0 wt. %. In this regard, thermodynamic calculations of the double AP/ PE mixture (where AP is ammonium perchlorate) were carried out.

Currently, there are a large number of chemical compounds, both organic and inorganic, which are used to create gas-generating compositions [3, 4]. PE can be used as a fuel for gaseous mixtures based on potassium chlorate [5]. Compositions based on perchlorates with PE have high energy characteristics and burn stably at normal pressures. Compositions based on sodium and potassium nitrate in comparison with chlorates and perchlorates, have a lower energy level.

Recently, gas generator compositions based on perchlorates with hydrocarbons ($C_xH_y$) have been widely used [6, 7]. Polymers such as PE, polypropylene, PET are used as hydrocarbons in these compositions. Another advantage of these compositions is the ability to prepare them directly on the job site, which in turn improves labor safety [8].

It was previously established [9, 10] that pyrotechnic gas-generating compositions based on ammonium perchlorate (AP) or potassium perchlorate have optimal thermodynamic and ballistic characteristics at a relatively low combustion temperature. The recommended oxidizing agent content is 80% by wt. This is due to the fact that when the content of AP in a smaller amount, there is a lack of oxidizing components, leading to a significant decrease in the burning rate. In the case of an increase in the amount of AP, the combustion process becomes unstable, which can lead to abnormal operation of the paragenerating compounds. AP as a kind of oxidizing agent is widely used in composite energy materials and rocket fuels due to its advantages: high oxygen content, good physical and chemical stability [11, 12].

Based on the individual properties of the components, it can be difficult to determine whether a substance is suitable for use as an oxidizing agent, fuel, binder, phlegmatizer, cooling or active additive to create a new gas-generating composition. In turn, testing the combinations of selected components in practice is a time consuming task. Therefore, thermodynamic modeling of combustion processes is a necessary tool for the selection of the composition of the combustible mixture [4].

Thermodynamic calculations can be performed by means of TDS software package [13]. It allows you to calculate the thermodynamic properties of complex chemically reacting or inert systems of any elemental composition both under conditions of complete thermodynamic equilibrium and with partial freezing. Both the initial reagents and the products can be multiphase and multicomponent mixtures, consisting of substances with different states of aggregation. As a result of the calculation, all equilibrium parameters, thermodynamic properties, as well as the phase composition of the products and the chemical compositions of each of the phases present in the products are determined [13].

Synchronous thermal analysis combines thermogravimetry (TG) with the Differential Scanning Calorimetry (DSC) in a single measurement [14]. TG is based on continuous recording of the change in the mass of the sample as a function of time or temperature during heating in accordance with a selected temperature program in a given gas atmosphere. The measuring system allows the sample to be repeatedly heated and cooled at a controlled rate as well as to carry out isothermal measurements. The method provides information on the temperatures and heats of phase transitions (melting, crystallization, glass transition), thermodynamics and kinetics of chemical reactions, chemical composition, purity, thermal and oxidative stability of various materials, etc. The method is widely used for research of chemical compounds, polymer and composite materials in various branches of science and technology.

The method of synchronous thermal analysis (STA) is based on the simultaneous continuous recording of changes in the corresponding characteristics of the sample (due to phase transitions or chemical reactions) depending on time or temperature in accordance with the selected temperature program in a given gas atmosphere [15]. The main advantage of STA - the simultaneous use of TG and DSC - is the ability to obtain more information than using two separate instruments. Since the experimental conditions for TG and DSC signals completely coincide (the same atmosphere, flow rate, vapor pressure of the sample, heating rate, thermal contact with the crucible and sensor, radiation, etc.), two or more data sets are available at any time. Describing the behavior of the sample. This makes it possible to qualitatively improve the analysis of signals, for example, it makes it possible to distinguish a phase transition from a decomposition reaction, an addition reaction from condensation, a pyrolysis reaction, oxidation and combustion, etc. STA provides information on the composition, thermal and oxidative stability of materials, phase transitions, temperatures and kinetics of chemical reactions. The method is widely used in scientific and industrial laboratories [17].

Currently, there is a lot of research on the thermal analysis of AP [19-22]. However, the behavior of AP in a mixture with PE has not been studied. Thus, conducting experiments on thermal analysis of the perchlorate+PE composition is an important task.

The purpose of this work is to develop gas generator compositions that are applicable without the addition of additional components for splitting block stone in a gentle mode or breaking hard mineral rocks. The search for optimal gas generator compositions was carried out by comparing the results of thermodynamic modeling and synchronous thermal analysis of the decomposition of AP, including in a pair with PE.

## THERMODYNAMIC MODELING

### The Basics of the Experiment and the Main Results

In this research thermodynamic calculations were conducted using the TDS software package [13]. To carry out thermodynamic modeling of combustion, the HP-problem was solved by the method of extremum of characteristic functions, embedded in the TDS software package.

A mixture of AP+PE in various ratios of fuel and oxidizer have been chosen. In the studied mixture of AP+ PE, the fuel content varied from 5.0% to 15.0%. The calculation was carried out at atmospheric pressure. Determination of the combustion temperature of gas-generating compositions is of great importance, since it is a criterion for assessing existing ones and facilitates the creation of new, more advanced compositions. As a result of thermodynamic modeling, the following thermodynamic characteristics of gas-generating compositions based on AP were determined: gas capacity W, combustion temperature, heat of combustion, molar mass of gases, operability RT, and content of condensed phase in combustion products. The results of calculating the combustion temperature, the volume of gaseous products are shown in Figures 1, 2 in the form of dependences on the excess fuel ratio.

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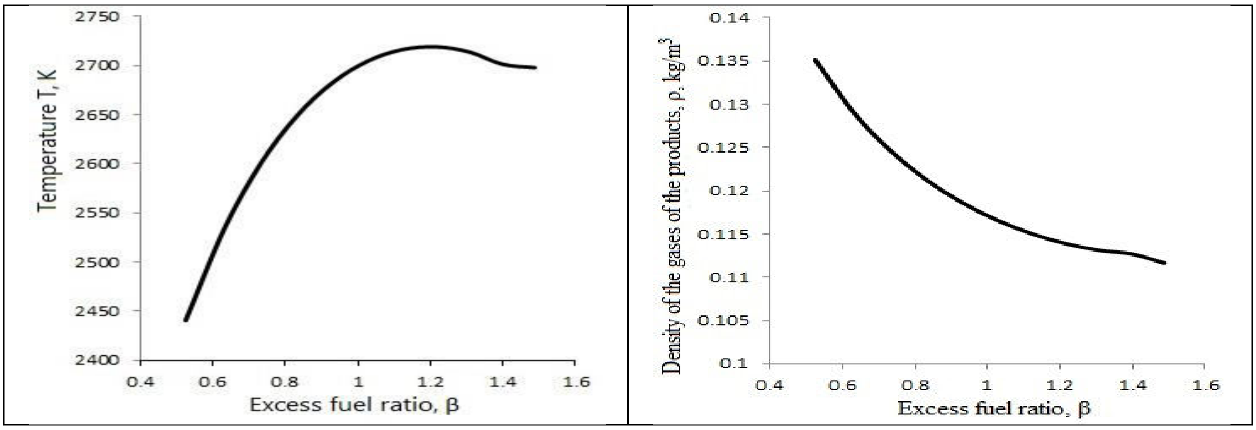


**Figure-1.** Graphs of the dependence of the temperature T, the density of the gases of the products ρ on the excess fuel ratio β in the composition of AP+PE at atmospheric pressure.

As can be seen from Figure-1 that at a stoichiometric ratio (90% AP and 10% PE), a maximum combustion temperature of about 2700 K and a significant yield of combustion products are achieved.

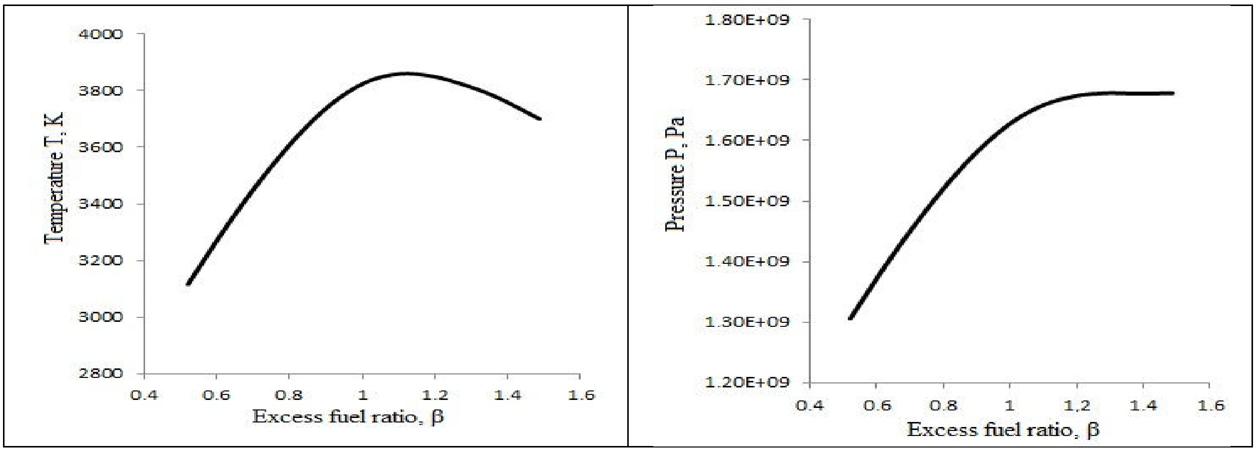


**Figure-2.** Graphs of the dependence of temperature T, pressure p on the excess fuel ratio β in the composition of AP+PE in a closed space.

Polymer (PE) was chosen as a fuel, the choice in favor of this component is due to the fact that AP readily interacts with PE, and this fuel contributes to the rapid decomposition of AP [14].

AP decomposition reaction:

$$2NH_4ClO_4 \rightarrow N_2 + Cl_2 + 2O_2 + 4H_2O \quad (1)$$

PE oxidation reaction:

$$(C_2H_4)_n + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad (2)$$

From this, the total reaction of the double mixture of AP+PE is:

$$12NH_4ClO_4 + 5(C_2H_4)_n \rightarrow 12HCl + 28H_2O + 10CO_2 + 6N_2 \quad (3)$$

Table-1 indicates that the main combustion products are $H_2O$, $N_2$, HCl, $CO_2$. Thus, it can be concluded that the optimal composition for gentle destruction of concrete blocks or rocks corresponds to a stoichiometric mixture of AP and PE.

Also, the UV-problem was solved for the composition of AP+PE in a closed volume. The fuel content varied from 8% to 17%. The calculation results are shown in Figure-2 graphically in the form of dependences of temperature (a) and pressure (b) on the excess fuel ratio.

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**Table-1.** Calculated composition of gaseous combustion products of a double mixture of AP + PE.

| Products | Products content, % | | | | | | |
|---|---|---|---|---|---|---|---|
| **$H_2$** | **2.4048** | **3.4560** | **4.6090** | **14.4727** | **27.4462** | **38.7436** | **47.1121** |
| CO | 4.0291 | 5.8504 | 7.6829 | 17.8274 | 25.0447 | 29.7052 | 33.4881 |
| HCl | 16.8655 | 16.5391 | 16.3266 | 15.6234 | 13.8227 | 11.6486 | 9.8763 |
| $N_2$ | 9.9740 | 9.7331 | 9.5128 | 8.25512 | 6.9461 | 5.8246 | 4.9369 |
| $H_2O$ | 42.9608 | 42.5215 | 41.8899 | 34.3294 | 22.4141 | 11.2535 | 2.6202 |
| $CO_2$ | 10.8504 | 10.7061 | 10.3231 | 6.6246 | 4.0463 | 2.8195 | 1.6984 |
| $CH_4$ | 2.87E-13 | 1.10E-12 | 3.30E-12 | 4.92E-10 | 5.60E-08 | 2.09E-05 | 0.2657 |
| $Cl_2$ | 3.5434 | 3.3134 | 3.0095 | 0.9182 | 0.0699 | 0.0009 | 5.47E-07 |
| $O_2$ | 4.3871 | 2.8101 | 1.7571 | 0.0332 | 3.23E-05 | 4.51E-10 | 1.64E-18 |
| NO | 0.4809 | 0.4015 | 0.3217 | 0.0326 | 0.0004 | 2.54E-07 | 7.35E-13 |
| The coefficient of excess of flammability | 0.8141 | 1.0045 | 1.2067 | 1.4037 | 1.6127 | 1.8103 | 1.9975 |

We can observe a high combustion temperature of about 3800 K and a pressure of about $1.6 \cdot 10^9$ Pa which corresponds to an explosion in a closed volume (Figure-2). Pyrotechnic compositions of gas generator cartridges are characterized by the following parameters: performance of combustion products or RT, W. These characteristics are the determining factors in the development of gas-generating pyrotechnic compositions (Figure-3). As follows from Figure-3, the values of RT and W reach a maximum at a stoichiometric ratio of oxidizer to fuel, RT is about 820 kJ / kg and W is in the region of 1025 L / kg, this once again proves that the composition was prepared correctly.

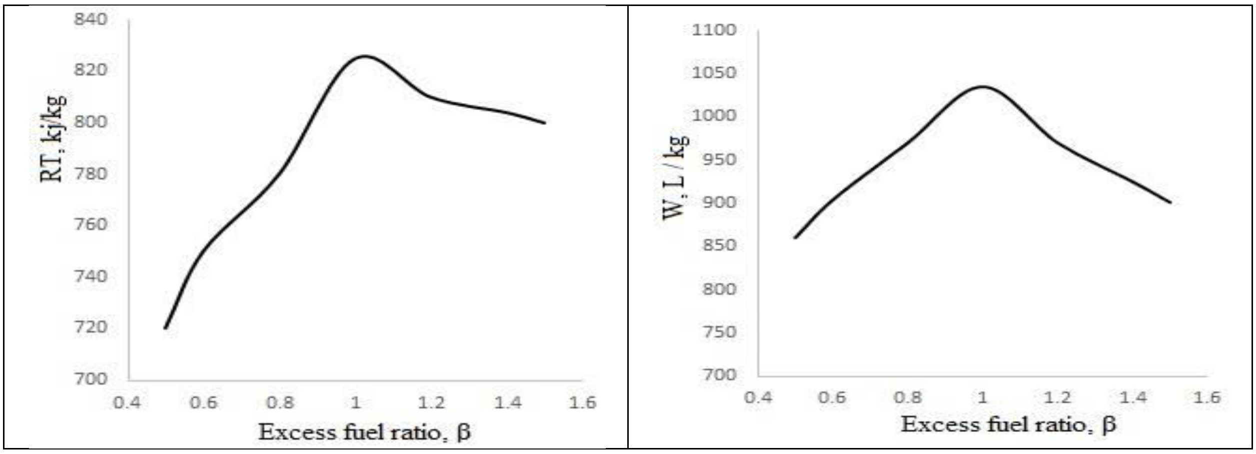


**Figure-3.** Dependence of performance and specific gas production on the excess fuel ratio.

**Synchronous Thermal Analysis**

There are many works that describe the thermal analysis of AP [19-23]. As the behavior of AP in a mixture with PE has not been well studied that studying thermal analysis of the perchlorate+PE composition is a relevant task.

To study the effect of the oxidizing agent AP on the energy release of composite energetic materials, the thermal decomposition of AP and AP+PE was studied by TG-DSC [18].

In this work, a Netzsch STA 409 PC device was used for simultaneous thermal analysis of the AP samples and the AP+PE mixture. The weighed portion of AP+PE was 8.6 mg, pure AP was 10 mg, and the heating rate was 10°C / min.

The obtained curves of DSC and TG of AP+PE are shown in Figure-4. For comparison, the same figure shows the DSC curve and the TG curve of pure AP. The presented TG (Figure-4) shows a gradual decrease in weight to 96.00%. AP+PE, for pure AP weight reduction was 99%. It should be noted that when carrying out experiments to determine the thermokinetic parameters of the decomposition of AP and AP+PE, the residual mass in the crucible is about 1.0-4.0 % by wt. of the original sample.

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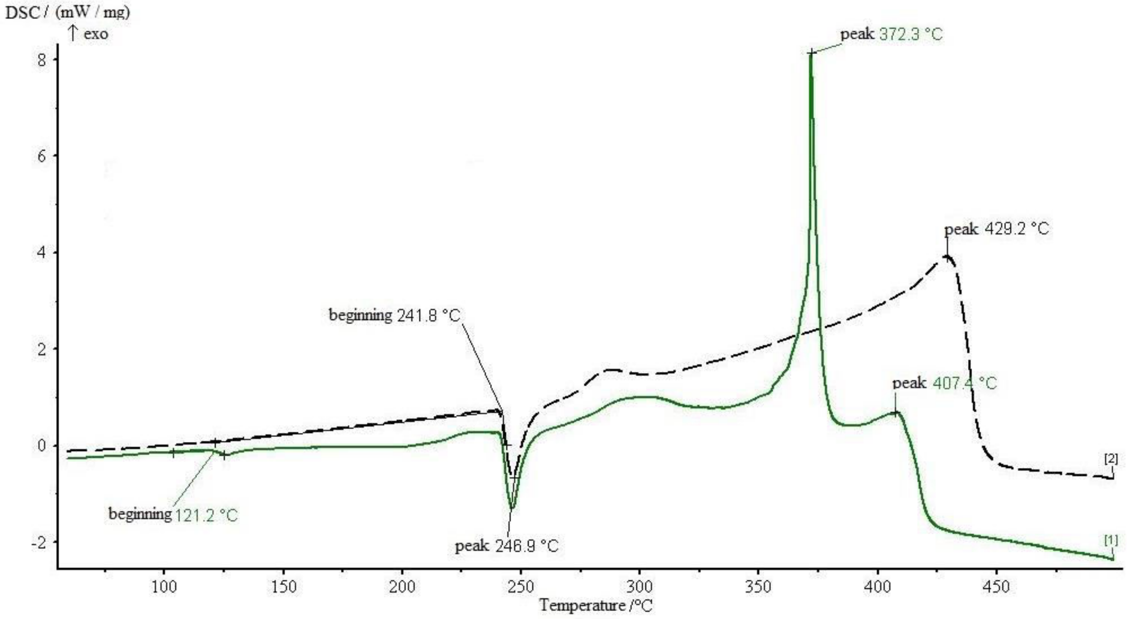
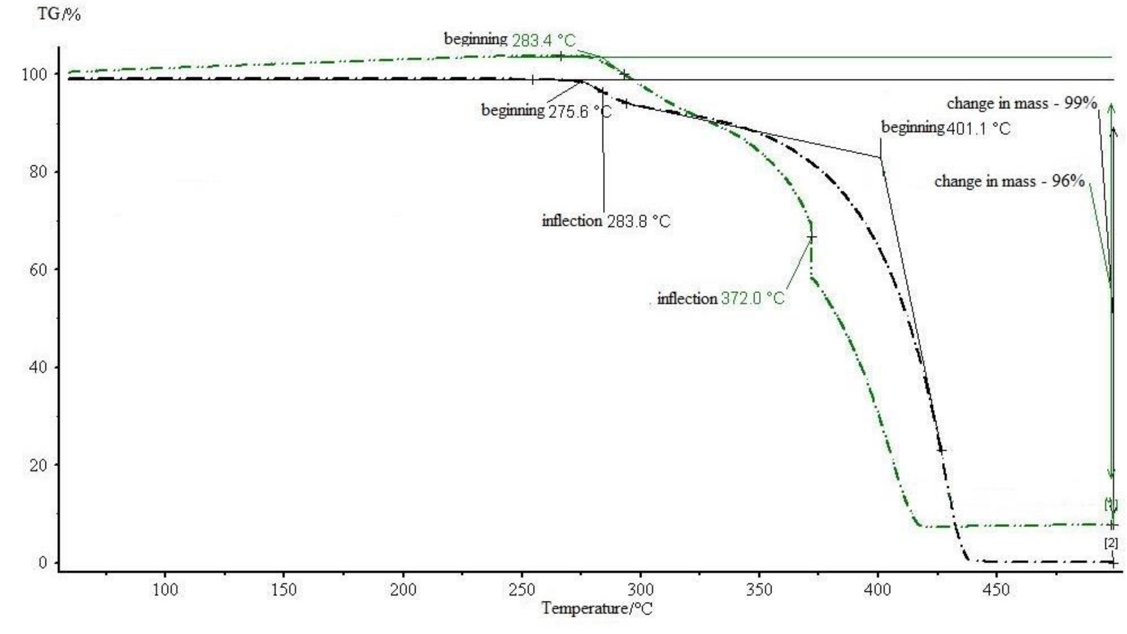
It should be noted that at temperatures around 241°C (514 K), an endothermic peak is observed corresponding to a polymorphic transition in the crystal structure of AP, in both cases the peaks coincide. At a temperature of about 372.3 °C (645.3 K), an exothermic peak can be seen, at which the oxidation of PE occurs with a large release of energy. The peak at 429.2°C (702.2 K) corresponds to the decomposition of AP.




(a)




(b)

**Figure-4.** TG and DSC curves of the thermal decomposition of AP in pure form (a), as well as with the addition of PE (b) at a heating rate of 10°C / min in a nitrogen atmosphere.

**CONCLUSIONS**

Thermodynamic calculations of the combustion parameters of gas-generating compositions were carried out to determine the optimal amount of the initial components of the composition. It has been established that the greatest serviceability and specific gas productivity are observed in the area of stoichiometric ratio of the initial components of gas generator compositions. Thermal analysis was performed to investigate the thermal behavior of ammonium perchlorate and a mixture of ammonium perchlorate and polyethylene using TG-DSC method. The developed gas generator composition based on ammonium perchlorate can be used for open pit mining for splitting block stone in a gentle mode or breaking hard mineral rocks. This composition is safe from an environmental point of view; the composition of the products does not contain poisonous gases such as carbon monoxide and nitrogen oxides.

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