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ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

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«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
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ZH. K. YELEMESSOVA[1,2], R. SHEN[3]

[1]Al-Farabi Kazakh National University, Almaty, Republic of Kazakhstan,
[2]Institute of Combustion Problems, Almaty, Republic of Kazakhstan,
[3]Nanjing University of Science and Technology, Nanjing, China.
E-mail: yelemessova.zh@gmail.com

METAL-ORGANIC FRAMEWORKS BASED ENERGY PROPELLANT: EFFECT ON COMBUSTION OF AMMONIUM NITRATE AND MAGNESIUM COMPOSITION

Abstract. In order to obtain a better understanding of thecombustion characteristics of ammonium nitrate (AN) andcarbon (C) mixtures (AN/C), burning tests and Differential Scanning Calorimetry (DSC) were performed.Ammonium nitrate is widely used in rocket fuels, in explosives and gas generators as an oxidant. However, several major drawbacks have reduced the scope of the application.In order to improve these disadvantages of AN in the composition of composites, energy materials useactivated carbonwith metal oxidesas a metal organic frameworks (MOFs). In addition, the influence of copper oxide on the combustion of compositions and its thermal characteristics was studied.Compositions were combusted at the pressure of 1 MPa, 2 MPa, 3 MPa and 3,5 MPa in the combustion chamber and the burning rates were determined.With the addition of a metal oxide, burning rate has increased for 2–3 times.The thermal characteristics of compositionswere analyzed using DSC at different heating rates, andthe activation energy of the system was calculated.

Key words: Energetic materials, ammonium nitrate, activated carbon, copper oxide, burning rate, activation energy.

Introduction. Energy materials have several advantages: (1) do not consume oxygen from the environment (chemical transformation reactions occur due to internal oxygen resources; (2) it is possible to control the rate of a chemical reaction in a rather wide range from burning to explosion (10-5 seconds); (3) allow in the shortest possible time to obtain large amounts of the required energy for the target application. The above listed advantages continue to attract the attention of researchers for more than a hundred years, the results of previous work in this area have opened up access to the development of technical progress that we have today.

Metal–organic frameworks (MOFs) have attracted great attention because of their intriguing molecular topologies and potential applications in chemical separation, gas storage, drug delivery, catalysis and chemical sensor technology. Particularly, MOFs could also be potential energetic materials because of their high densities and high heats of detonation.The porous crystalline structure attracts attention due to its high specific surface characteristics and the possibility of changing their physicochemical properties by introducing metal centers [1]. However, the process for preparing these bulk polymers is expensive and multistage. In this connection, it is of interest to search for alternative methods for obtaining bulk materials, one of which are structures based on graphene oxide

frameworks and activated carbon materials. The growing popularity of multilayer graphene's is due to the uniqueness of their physical and chemical properties. A promising, simple and cost-effective method is the production of activated carbon materials from plant wastes like rice husk or walnut shell [1-3].

Ammonium nitrate (AN) is widely used as a fertilizer and as an ingredient in industrial explosives or oxidizing chemicals because it is relatively cheap, releases almost 100% gaseous products when it reacts, and has a positive oxygen balance (+20.0%).Recently, AN-based compositions have been investigated for use as oxidizers of rocket propellants and gas generators for air bags, because AN does not contain toxic halogens. However, AN has several disadvantages, such as a low combustion performance, high hygroscopicity, and solid-state phase transitions at temperatures below 100^{o}C. Many combinations of combustible contents and additives with AN have thus been explored in an attempt to improve these properties [4, 5]. For example, AN-based compositions with metal oxides are beneficial with respect to burning rate and hygroscopicity [6,7]. However, while these studies have demonstrated the thermal properties and structures of mixtures of AN with metal oxides, evolved gas analyses have not been carried out.

Understanding the thermal characteristics of AN and mixtures of AN with combustibles and additives is necessary for enabling its general use in potential new applications, such as propellants and gas generators. Consequently, this study aimed to understand the mechanism of decomposition of AN-based mixtures, with an emphasis on the analysis of the gases that evolve from AN, carbon, and copper oxide (CuO) mixtures. Carbon is a typical combustible material, but there are many different forms of carbon with different physical properties [8-10].

The purpose of this study is to evaluate the influence of carbon properties on the combustion of AN/C and to clarify the relationship between combustion and the thermal decomposition of AN/C.

EXPERIMENTAL

2.1. Materials and Propellant Samples. Activated carbon was obtained in the Laboratory of Functional Nanomaterials of the Institute of Combustion Problems, Almaty, Kazakhstan. Mechanical treatment (15 min) of ammonium nitrate (purity 99%) powder was carried out in a planetary mill. Ammonium nitrate was used as an oxidizer in the condensed mixture with a diameter of 212-250μm. Magnesium (Mg) was used as a fuel, and its diameter was 200μм. The diameter of the metal oxide particles was 60-70 μm, and it acted as a catalyst. Nitrate cellulose was used as a binder.

2.2. Measurement of Burning Characteristics. The diameter of compositions is 6 mm and the length is10 mm. The process of combustion was studied under gas pressure in the combustion chamber. Each sample was heated up and ignited with nichrome wire. Each of the samples is ignited under a pressure of 1-3,5 MPa. The combustion of compositions was registered using high-speed cameras. These recorded videos were used to determine the burning rate. The degree of measu-

rement error of 0.01 mm is measured from the dependence of the height of the surface combustion.

All measurements were made 3 times under pressure and were calculated using the average burning rate. If 1/3 of the sample is not ignited or does not burn the burning rate is not determined. Figure 1 shows the equipment for practical work.

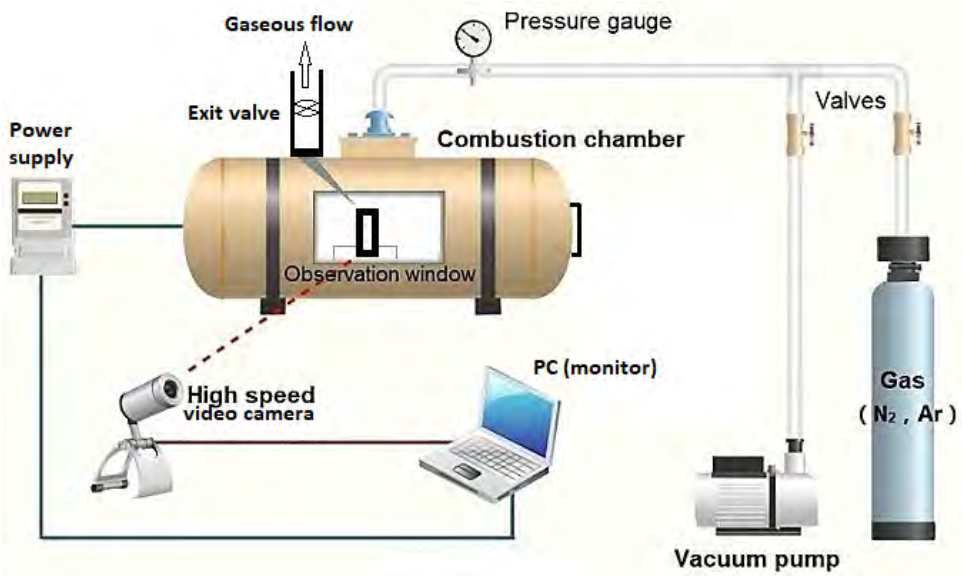


Figure 1 – Scheme of the combustion chamber under pressure

2.3. Measurement of Thermal Decomposition Behavior. Thermal analysis is a fast and effective method for studying thermal fires of energy materials. The description of the thermal decomposition was investigated in a Differential Scanning Calorimeter in temperature intervals from 30°C to 550°C.The equipment operates in atmospheric pressure in a stream of nitrogen (300 cm^3/min). DSC-TG is working with the heating rate of (β) 5–20 $K \cdot min^{-1}$.In DSC-TG equipment, the standard line of DSC-TG was measured four times for each sample.

RESULTS AND DISCUSSION

3.1. Combustion characteristics. Figure 2 shows the mechanism of combustion of AN/Mg composites in the combustion chamberat a pressure of 1 MPa, 2 MPa, 3 MPa and 3.5 MPa and depending on the increase in pressure the increases in burning rate in the form of a line.

Figure 3 shows the mechanism of combustion of AN/Mg/C composites in the combustion chamberat a pressure of 1 MPa, 2 MPa, 3 MPa and 3.5 MPa.

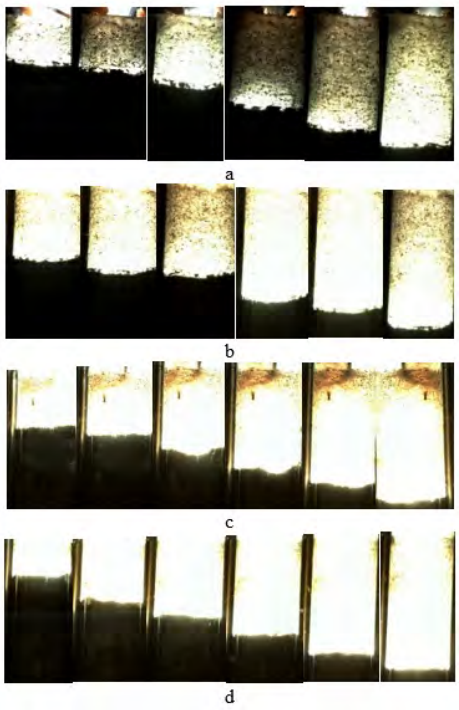


Figure 2 – Burning images of AN/Mg composites at pressures (a) – 1 MPa, (b) – 2 MPa, (c) – 3 MPa and (d) – 3.5 MPa

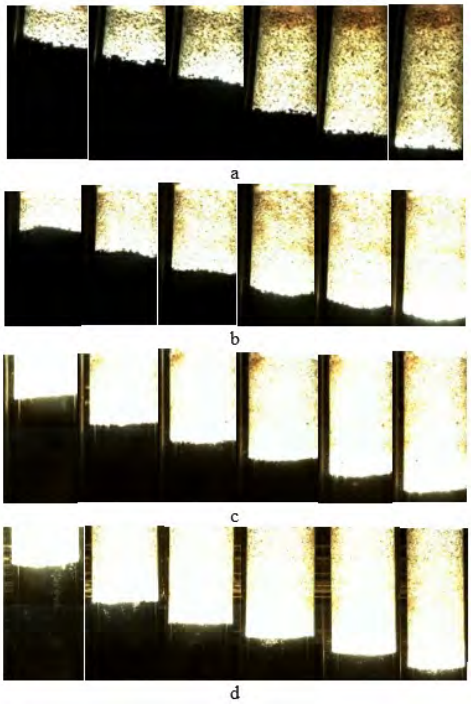


Figure 3 – Burning images of AN/Mg/Ccomposites at pressures (a) – 1 MPa, (b) – 2 MPa, (c) – 3 MPa and (d) – 3.5 MPa

And a linear increase in combustion rates due to a linear increase in pressure on composites AN/Mg/C. Compared with the AN/Mg system, the lower pressure limit was reduced, and the burning rates increased the catalytic effect of activated carbon. In addition, some of the disadvantages of ammonium nitrate have been added. According to the experimental results, it can be seen that the propellants are completely burned at high combustion rates.

Figure 4 shows the mechanism of combustion of AN/Mg/C/CuOcomposites in the combustion chamberat a pressure of 1 MPa, 2 MPa, 3 MPa and 3.5 MPa.

In figure 4 also increases in burning rate due to increases in pressure for AN/Mg/C/CuO. Compared with the AN/Mg system, the PDL was loweredand the burning rates increased by the catalytic effect of CuO.

Characteristics of the burning rates of composite propellants AN/Mg, AN/Mg/C and AN/Mg/C/CuO at different pressures are shown in figure 5.

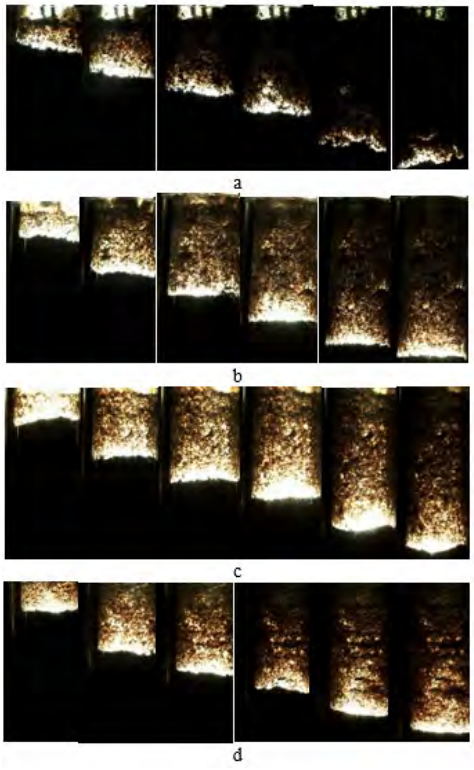


Figure 4 – Burning images of AN/Mg/C/CuOcomposites at pressures
(a) – 1 MPa, (b) – 2 MPa, (c) – 3 MPa and (d) – 3.5 MPa

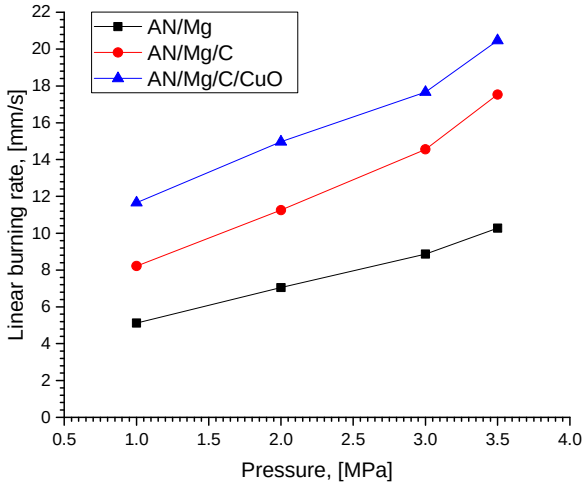
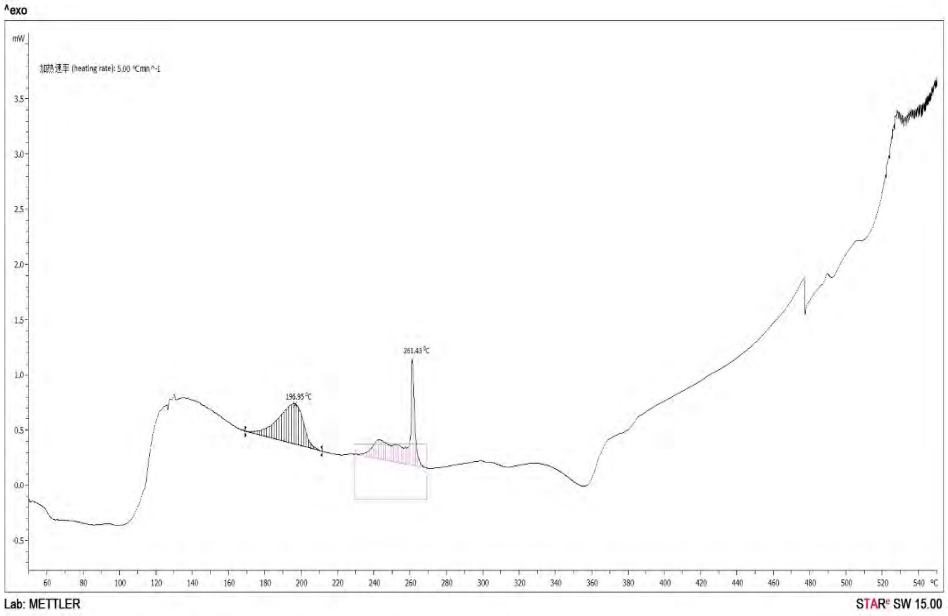


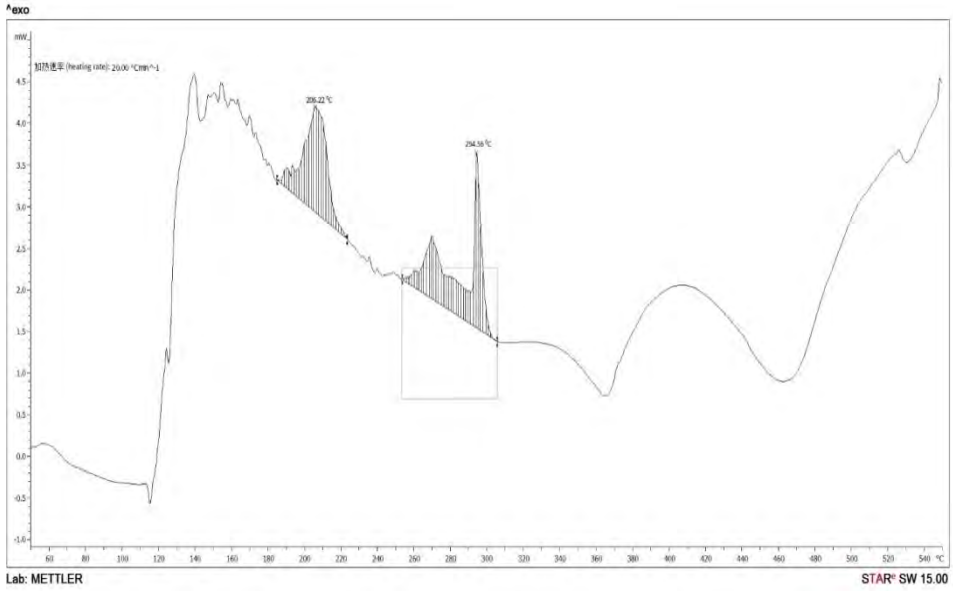
Figure 5 – Dependencies of the burning rates
of composites AN/Mg, AN/Mg/C and AN/Mg/C/CuO on the pressure

When adding carbon and CuO, the burning rate of the propellant composites increases by 3 mm·s^{-1} in average at each pressure.

3.2. Characteristics of thermal decomposition. The characteristics of the heat discharge of composites, prepared in different ways, were measured at different heating rates by the DSC method. Figure 6 shows two exothermic peaks at



a



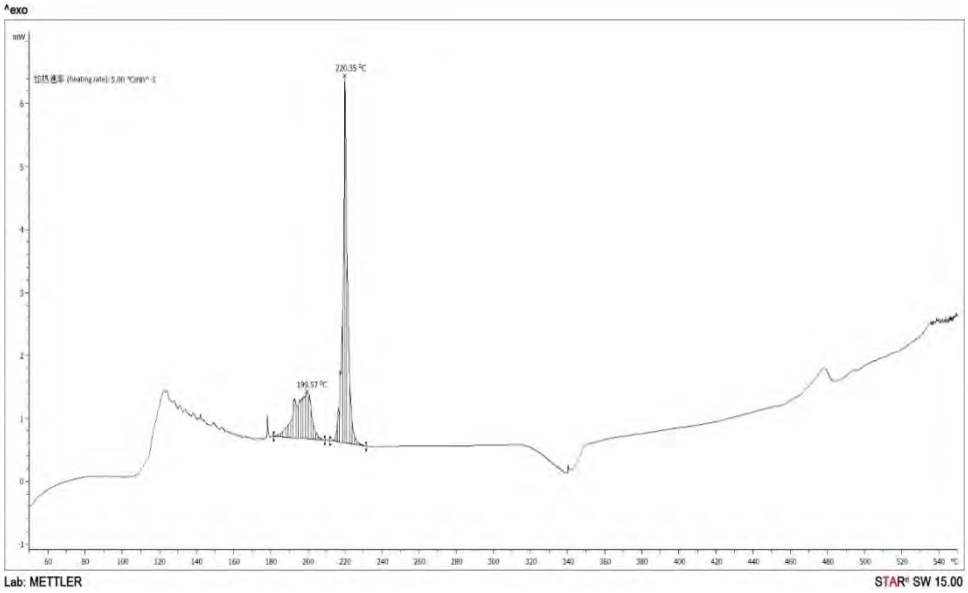
b

Figure 6 – DSC curves measured at (a) β=5 and (b) β = 20 K min–1 forAN/Mg

196.95°C and 261.43°C, starting from 165°C to 267°Coccurs the main decomposition of ammonium nitrate:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O + Q. \quad (1)$$

When activated carbon was added, a sharp decrease in heat absorbed by the sample was noticeable from 261.43°C to 220.35°C (figure 7). With the addition of



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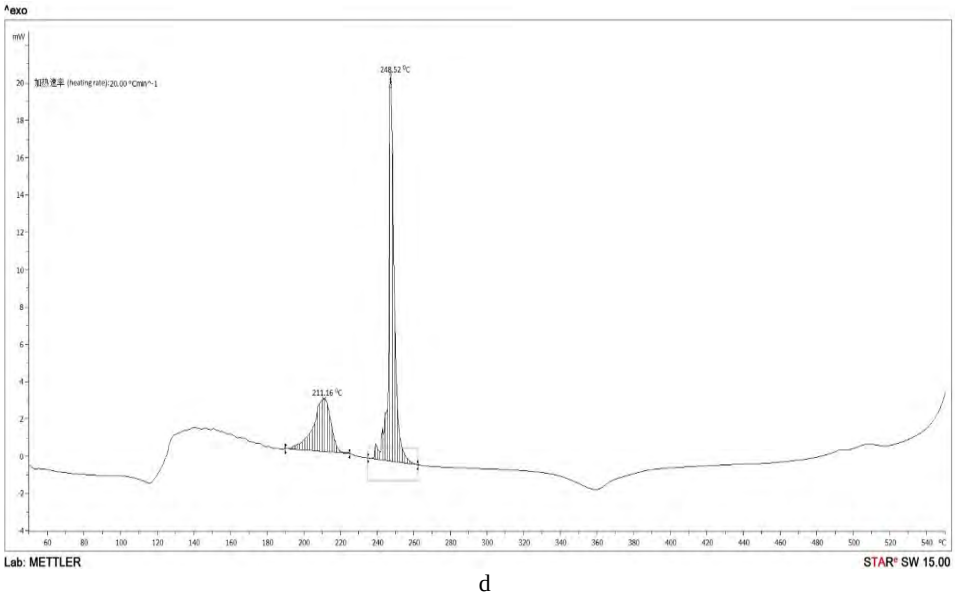
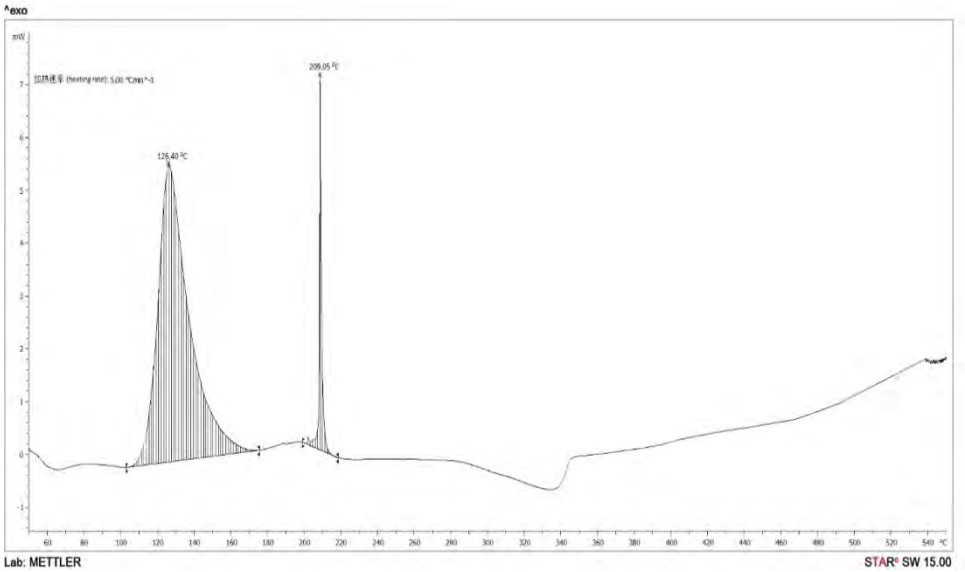
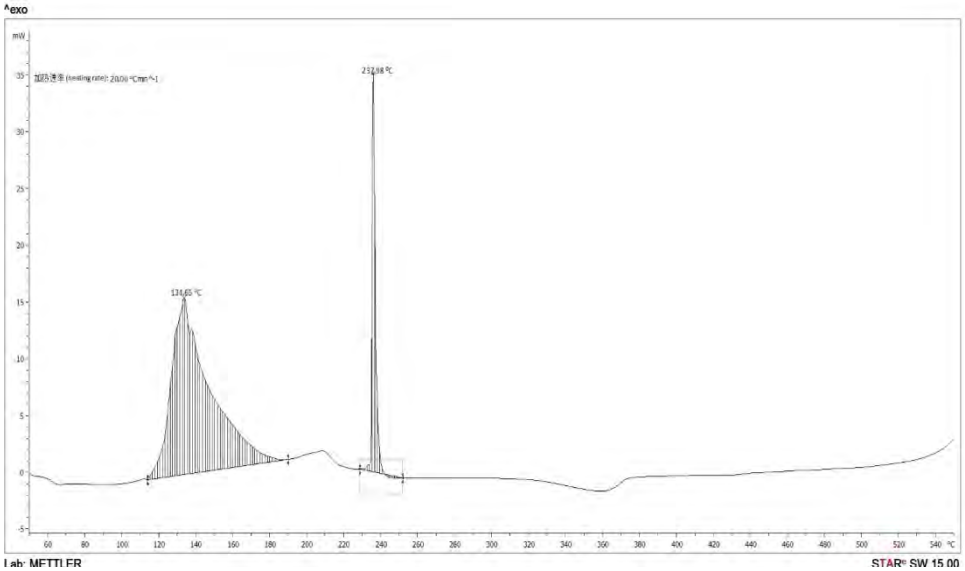


d

Figure 7 – DSC curves measured at (c) β=5 and (d) β = 20 K min–1 forAN/Mg/C



e



f

Figure 8 – DSC curves measured at (e) β=5 and (f) β = 20 K min^{-1} forAN/Mg/C/CuO

CuO, the thermal decomposition temperature decreasedby 10^{o}C (figure 8). The addition of copper oxide to ammonium nitrate may affect as a catalyst to AN.

Based on the obtained results of DSC, it can be concluded that activated carbon has a direct impact on the process of thermal decomposition of ammonium nitrate, reducing the temperature of complete decomposition and the reaction rate. It is established that the addition of activated carbon from affects the temperature change of phase transitions during the decomposition of ammonium nitrate.

3.3. Kinetics of thermal decomposition. The activation energy is important in the kinetics of thermal decomposition and is evaluated using the Kissinger method based on the DSC analysis. This method is widely used and does not requirea detailed reaction model. The activation energy (E_a) is calculated from the total physical energy of the thermal decomposition and the total amount of activation energy of the chemical reaction, and some researchers have studied the activation energy of composite rocket fuel and solid high-energy materials using the Kissinger method [11, 12].

According to the Kissinger method, E_a is expressed by the following equation:

$$\frac{E_a}{R} = \frac{dln(\beta T_p^{-2})}{dT_p^{-1}} , \quad (2)$$

where T_p - is the peak temperature of the DTA curve. E_a- can be calculated from the slope of the plot of $\ln(\beta T_p^{-2})$ against T_p^{-1}. E_a can be expected to vary when T_p on the DSC curve changes with the addition of the catalyst.

The values of composites can be determined by the DSC values measured at each heating rate in determining the activation (E_a) of gas generators with β = 5, 10, 15 and 20 $K \cdot min^{-1}$. Table 1–3 shows the calculated activation energy (E_a) according to the Kissinger method.

Table 1 – Calculation of the activation energy (E_a) according to the Kissinger method for the composition AN/Mg

T_{max}, °C	$1/T_{max}$	Heating rate, K/min	ln(β/T^2)
261.43	1.870627	5	-9.52688
276.05	1.820830	10	-8.94216
283.52	1.796396	15	-8.58991
294.56	1.761463	20	-8.37838
	slope	-10.8327	
	E_a	90062.32	J/mol
		90.06	kJ/mol

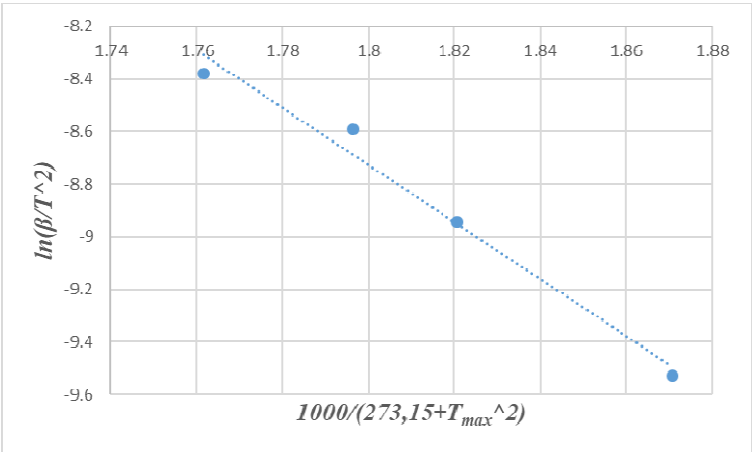


Figure 9 – Kissinger plot of AN/Mg composition

Figure 9 presents the results of calculations in the form of graphs reflecting the slope of the heating rate constant as a function of the variable obtained as the maximum decomposition temperature.As shown by the results of calculations, obtained experimental data, the activation energy of the composition AN/Mg was 90.06 kJ/mol according to the Kissinger method.

Table 2 – Calculation of the activation energy (E_a) according to the Kissinger method for the composition AN/Mg/C

T_{max}, °C	$1/T_{max}$	Heating rate, K/min	ln(β/T^2)
220.35	2.026342	5	-9.18661
240.60	1.946472	10	-8.66839
242.61	1.938886	15	-8.27949
248.52	1.916921	20	-8.03973
	slope	-9.9587	
	Ea	82795.65	J/mol
		82.80	kJ/mol

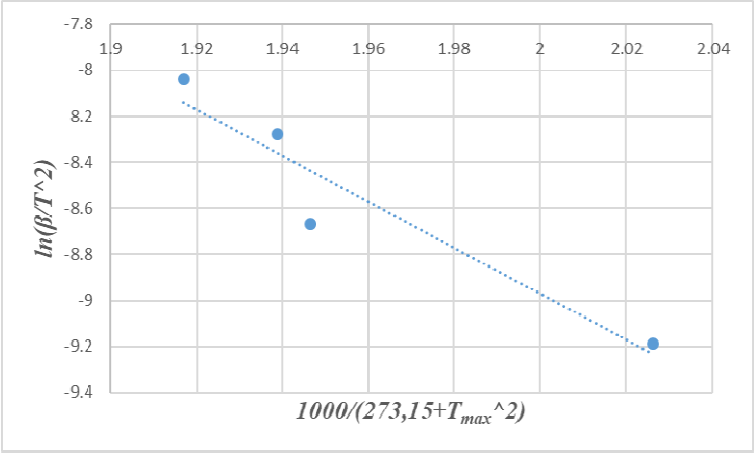


Figure 10 –Kissinger plot of AN/Mg/C composition

In figure 10, as shown by the results of calculations obtained from experimental data, the value of the activation energy of the composition of AN/Mg/C according to the Kissinger method was 82.80 kJ/mol.

Table 3 – Calculation of the activation energy (E_a) according to the Kissinger method for the composition AN/Mg/C/CuO

T_{max}, °C	$1/T_{max}$	Heating rate, K/min	ln(β/T^2)
209.05	2.073828	5	-9.08194
222	2.019590	10	-8.5083
229.26	1.990406	15	-8.16685
237.98	1.956449	20	-7.95345
	slope	-9.84678	
	E_a	81865.14	J/mol
		81.87	kJ/mol

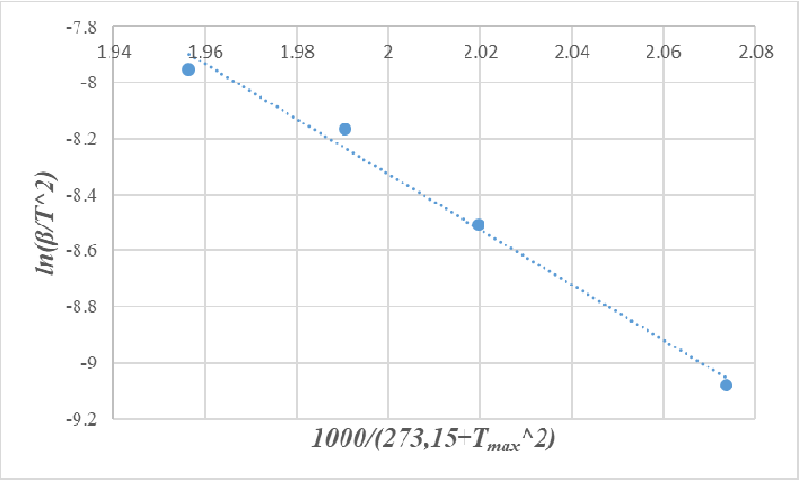


Figure 11 – Kissinger plot of AN/Mg/C/CuO composition

Figure 11 shows the results of calculations obtained from experimental data, the value of the activation energy of the composition of AN/Mg/C/CuO according to the Kissinger method was 81.87 kJ/mol.

The activation energy of composition AN/Mg thermal decomposition is reduced by adding C activated carbon and cupper oxide (CuO).These results show that the thermal decomposition of AN/Mg gas generator can be improved by C and CuO.

Conclusion. The using of the activated carbon as a fuel for the AN-based compositions increases the burning rate. Addition of CuO to AN/Mg/C increases the burning rate significantly. C and CuO additive reduce the activation energy of the AN/Mg composition from 90.06 kJ/mol to 82.80 kJ/mol and 81.87 kJ/mol. And improves the decomposition reactions in the condensed phase however, the main effect with the addition of CuO to the AN/Mg/C-based propellants can be assumed to take place in the gas phase reaction zone. CuO can be the catalyst for our AN-based propellant system.

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Резюме

Ж. К. Елемесова, Р. Шен

МЕТАЛОРГАНИКАЛЫҚ ҚҰРЫЛЫМ НЕГІЗІНДЕГІ ЭНЕРГЕТИКАЛЫҚ ОТЫНДАР: АММОНИЙ МЕН МАГНИЙ НИТРАТЫНЫҢ ЖАНУЫНА ӘСЕРІ

Аммиак селитрасы және көміртегі қоспаларының жану сипаттамаларын жақсы түсіну үшін дифференциалды сканерлеу калориметриясын қолдана отырып, жану сынақтары менталда улар жүргізілді. Аммиакселитрасызы мыран отынында, жарылғыш заттармен газгенераторларда тотығу құралы ретінде кеңінен қолданылады. Алайда, бір нешемаңызды кемшіліктері қолдану көлемін қысқартты. Композитті материалдармен энергетикалық материалдар құрамындағы аммонийнитратының көрсетілген кемшіліктерін жою үшін, металлоксидтері бар активтен дірілген көмірметалорганикалық негізретінде қолданылады. Сонымenқатар, мысоксидінің композицияның жануына әсері және оның жылу сипаттамаларыз ерттелінді. Композициялар жану камера сында 1 МПа, 2 МПа, 3 МПа және 3,5 МПа қысым мен жанып, жану жылдамдығы анықталынды. Металлоксидінің қосылуыменжану мөлшері 2-3 есеөсті. Композициялардың жылу сипаттамалары әртүрлі қыздыру жылдамдығындағы ДСК көмеі менталданды және жүйенің активтендіру энергиясы есептелінді.

Түйін сөздер: энергетикалық материалдар, аммонийнитраты, активтендірілген көмір, мыс оксиді, жанужылдамдығы, активтендіру энергиясы.

Резюме

Ж.К. Елемесова, Р. Шен

ЭНЕРГЕТИЧЕСКОЕ ТОПЛИВО
НА ОСНОВЕ МЕТАЛЛООРГАНИЧЕСКИХ КАРКАСОВ:
ВЛИЯНИЕ НА ГОРЕНИЕ СОСТАВА НИТРАТА АММОНИЯ И МАГНИЯ

Для лучшего понимания характеристики горения смесей аммиачной селитры и углерода, были проведены испытания на горение и анализы на дифференциальной сканирующей калориметрии (ДСК). Аммиачная селитра широко используется в ракетном топливе, во взрывчатых веществах и газогенераторах в качестве окислителя. Однако несколько основных недостатков сократили область применения. В целях устранения указанных недостатков аммиачной селитры в составе композиционных материалов, в энергетических материалах используют активированный уголь с оксидами металлами в качестве металлоорганических каркасов (МОФ). Кроме того, было изучено влияние оксида меди на горение композиций и его тепловые характеристики. Композиции сжигались в камере сгорания при давлении 1 МПа, 2 МПа, 3 МПа и 3,5 МПа и определены скорости горения. С добавлением оксида металла скорость горения увеличилась в 2–3 раза. Тепловые характеристики композиций анализировали с использованием ДСК при различных скоростях нагрева и была рассчитана энергия активация системы.

Ключевые слова: энергетические материалы, аммиачная селитра, активированный уголь, оксид меди, скорость горения, энергия активации.