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EXPERIMENTAL INVESTIGATIONS OF ENHANCEMENT OF COMBUSTION OF HAN-BASED PROPELLANT WITH K_2CO_3-ACTIVATED CARBON

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The article is dedicated to the 70th anniversary of Academician of International Higher Education Academy of Science, Professor, Dr.Sci. Zulkhair Mansurov. Prof. Mansurov is one of the founding fathers of modern nanoscience and combustion scince in Kazakhstan. It is great honor and pleasure to be a disciple and part of big school of Z.A. Mansurov.

Abstract
Burning 95% of by HAN-based propellant with carbonized rice husk treated by K_2CO_3were conducted in a pressure chamber at 10, 3 and 50 atmosphere initial pressure in a nitrogen media was investigated. The thermal and catalytic decomposition processes of HAN-based propellant with carbonized rice husk composition were carried out by differential thermal (DTA) and thermogravimetric analysis (TG). The study was conducted at a heating temperature of system ranging from 297 K to 723 K under nitrogen atmosphere at a flow rate around 100 ml/min in aluminum pans. DTA-TG analysis results showed that the initial temperature of HAN decomposition in the presence of the obtained RH-based AC is comparable to Iridium catalytic effect.

Key words: hydroxyl ammonium nitrate, thermal analysis, thermogravimetric analysis, the burning rate

1. Introduction

In the aerospace industry as liquid propellants, hydrazine used with the catalyst of iridium as a monopropellantmostly the type of fuel used in satellite control elements. Unfortunately, propellants based on hydrazine considered extremely toxic. Among the possible alternatives, hydrazine energy spread use of ionic liquids containing ionic oxidizer, fuel and water, whichcan be taken together as new monopropellants [1,2].

At the end of the twentieth century, water and energy connections have been proposed as: HAN (NH_3OHNO_3), HNF ($N_2H_5C(NO_2)_3$), ADN ($NH_4N(NO_2)_2$) etc., which are able to satisfy all the requirements of the propellant and their constituents. In a more general sense to use a combination of fuel rocket engines should have a reducing cation which is highly soluble and stable in aqueous solution, the oxygen balance fuels such substances is always positive.

In attempting to develop a new propellant, many compositions have been considered [3–5]. The recent formulation in Japan consists of HAN 73.6% - water, methanol and ammonium nitrate (AN) proposed by Hori Lab [6].

HAN - is a high-energy substance that has the prospect of becoming a substitute for hydrazine, so it becomes very popular in the field of propellants [7]. This material is less toxic, has a high density and performance superior to most energy-intensive materials used and is regarded as the primary oxidant for hybrid rockets. The main HAN-precursor is a "hydroxylamine - H_2NOH», OH group substitution product of one hydrogen atom of ammonia NH_3 in the molecule. Hydroxylamine and its salts are used to introduce the oxime group and hydroxamic acids as for the definition of carbonyl compounds. Sulfate used as the material for the manifestation of color films. The Hydroxylamine Perchlorate is widely used as an oxidant in solid rocket propellants, both independently and in admixture with other components [8]. From extensive studies, we can to characterize burning behavior of HAN and pressure effects on the burning rates and flame structures of HAN and HAN-based liquid propellants [8–14].

In this paper we will study the effect of Carbonized Rice Husk (CRH-475) on the combustion process of an aqueous solution of *HAN*, $NH_2OH*HNO_3$95% in the high-pressure chamber and a study of the kinetics of decomposition of the composition. According to the results of the litera-

ture review found very few studies that deal with the influence of carbon additives in this type of fuel. Our research directly related to the thermal and catalytic decomposition between the above mentioned substances. They will be presented and discussed the results of the impact ofCRH-475to decay and the physic-chemical properties of HAN.

The main purposes of research are: (i) determine the decomposition temperature and gas phase temperatures of HAN-based propellant by DTA-TG analysis; (ii) the burning rates of investigated formulations (iii) combustion temperatures at constant pressure, the effect of additives on the burning rates.

2. Experimental

2.1 Burning test

To investigate the burning rate used strand burner was developed in JAXA as part of research project. The chamber was filled with N_2 gas from a gas cylinder. The experimental sample is placed in the combustion chamber and pressed by the N_2 gas. Ignition delay, temperatures, pressures and burning process of HAN-based propellant with carbonized rice husk and recorded by Lab-view software (NI USB-6229) with the sampling rate of 1000 Hz. The accuracy of pressure sensor is ±0.5% FSO (Full Scale Output) which is equal to 0.076 MPa.To determine burning rate used the high-pressure chamber with a high-speed camera with the settings PHOTRON 250 frames per second and a resolution of 640h488 pixels. The experimental setup is shows in *Figure 1*. The experiments of combustion of HAN monopropellant with activated carbon from carbonized rice husk (CRH) was carried out in high pressure chamber by ignition with electric power at constant pressures from 10atm, 30atm and 50atm. Burning process of HAN-based combustion was taken by high speed video camera. The high pressure chamber placed compacted samples weighing 2 g, 1 cm in height and 6 mm in diameter. The two ends of the specimens were embedded with sensors for determining of burning rate by method of break point [1] that was connected to the oscilloscope. Upon reaching the required pressure level the initiation is performed by external electric power and a polymer binder GAP (glycidylazide polymer). The obtained results, to study of the burning rates HAN based propellants have been influenced by initial pressures.

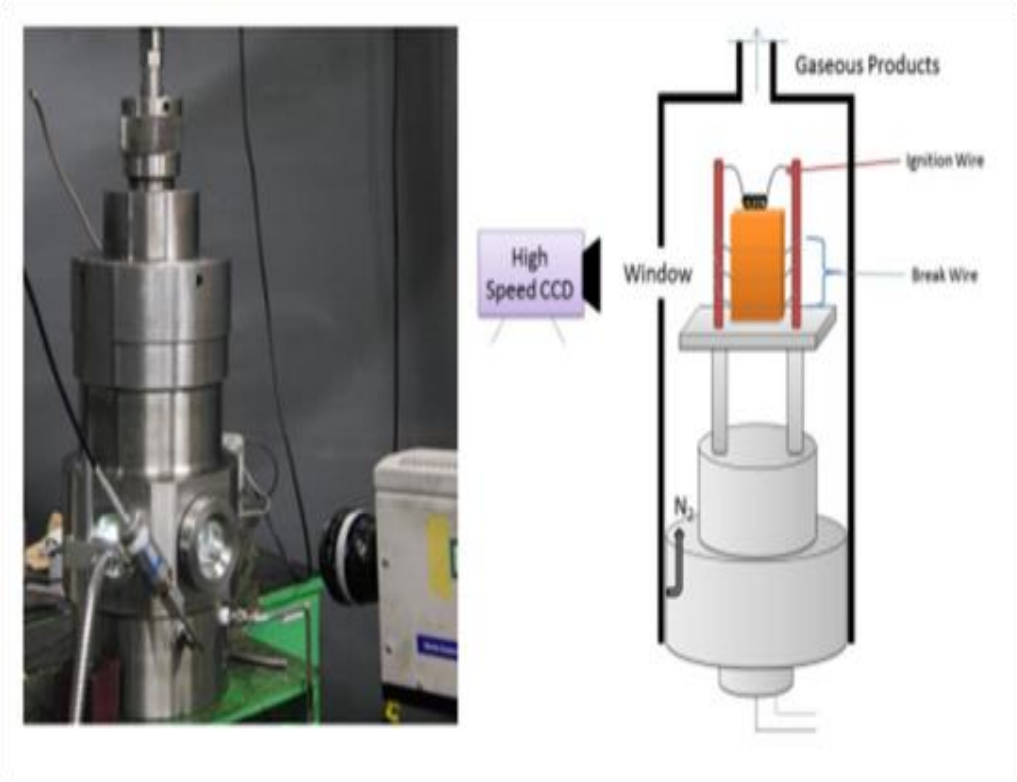


Fig. 1- Schematic of the experimental setup of the high pressure chamber

2.2 The differential thermal analysis

The thermal and catalytic decomposition of HAN-based propellant with carbonized rice husk were investigatedby thermal analysis apparatus and a batch reactor. Thermal analysis combines several methods of investigation after a TA, DTA methods TG-DSC. These methods allow solving diverse problems, such as the heat and the phase transition temperature of the test substances [12-13].The DTA-TGdates were recorded versus time, under argon flow (100 ml min^{-1}) and heating rates were fixed at 10°C min^{-1} for thermal decomposition and 1°C min^{-1} for catalytic decomposition. In this study it was used a modulated DTA apparatus operating at a temperature range between -180 and +725 °C and within ± 0.05 ° C and a heating rate of 0.1 to 25 ° C / min with a sample weighing 200 mg. In this work DTA-TG able to obtain the following info:(i) evaporation (endothermic peak); (ii) temperature of decomposition given by the inflexion point of the temperature curve; (iii) concentration of the HAN - based propelant at decomposition.

3. Results and discussion

The two different experiments carried out in this study can be divided by initial pressure conditions and heating rate.Firstly, investigations of the combustion of HAN-based as monopropellant with activated carbon was performed under external electric power at different pressure. Secondly, during the thermal analysis, the HAN based propellant with activated carbon was treated under gradual increase of temperature in different heating rates at 1 atm. The presented results were showed the possibility to apply high surface area activated carbon to enhance burning rate and decrease activation energy of HAN-based as green monopropellant which is used into space applications such as reaction control systems (RSC)

3.1 The combustion experiments in strand burner

In figure 2 presented different pictures of combustion tests of 95% HAN-based propellant with Carboxymethyl cellulose (CMC) taken by high speed video camera.

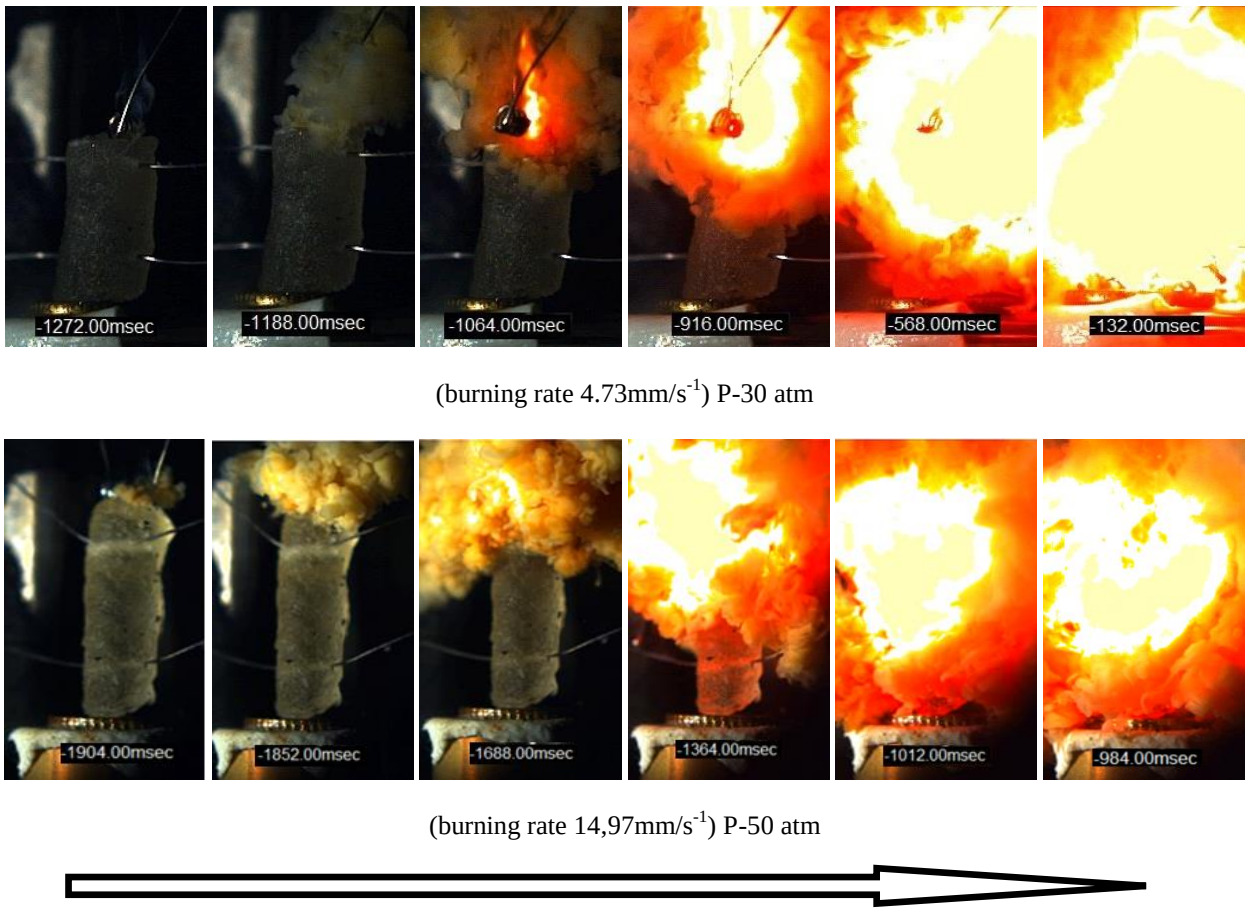
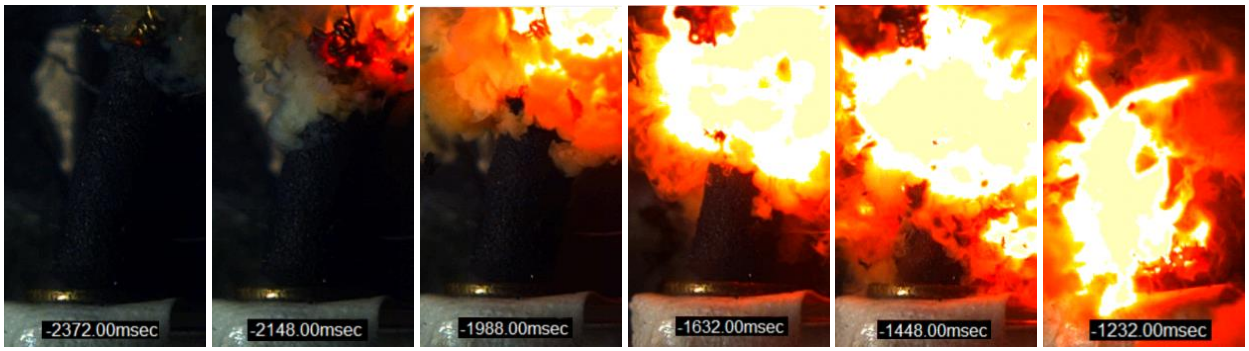


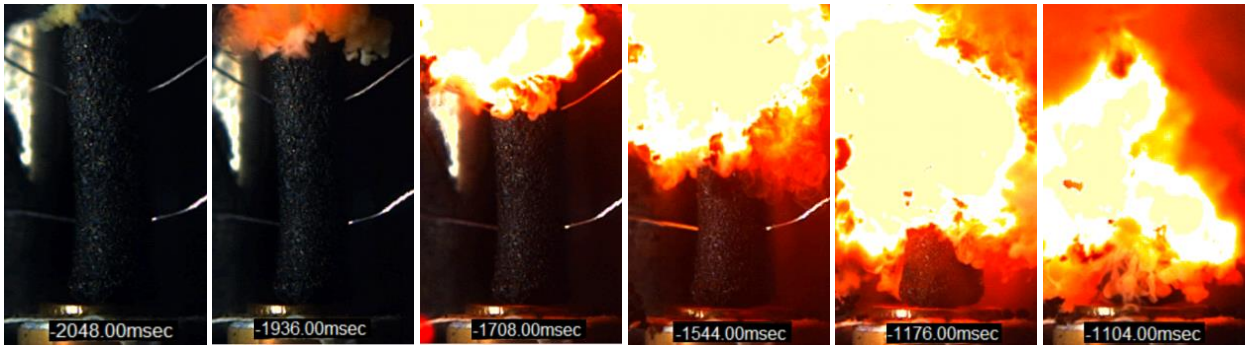
Fig. 2 - Combustion of 80% HAN-based propellant with 20% Carboxymethyl cellulose (CMC) at pressure of 10 atm., 30 atm. and 50 atm. in the strand burner

By the results of video shown the dynamics of combustion at pressures of 30 atm. and 50 atm. It should be noted that up to an initial pressure of 20 atm. ignition and burning of mixtures does not occur. According to the obtained results and literature data, the ignition,stable combustion and burning rates have been influenced by initial pressures. At 30 atm. initial pressure observed that the samples start to boil and generated brown bubbleswith generation of smoke, which indicates of the formation of NO_2 gas. Further follows ignition with a bright front of flame.

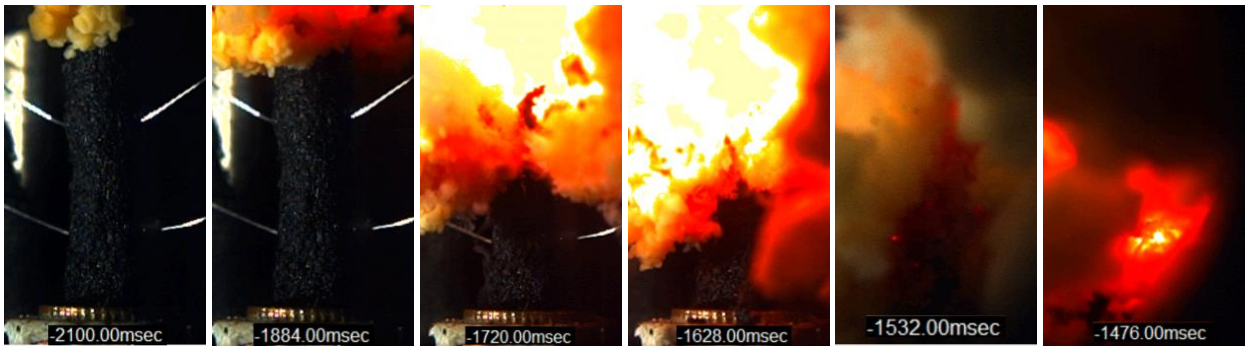
As seen in Figure 3, with the addition of activated carbon in the formulation at an initial pressure of 1 atmosphere is reached a stable combustion at a speed of 11 millimeters. Figure 3 shows different pictures of combustion tests of HAN / CMC with addition of Activated carbon (CRH) taken by high speed video camera.



(burning rate 11mm/s^{-1}) P-10atm



(burning rate 18.38mm/s^{-1}) P-30 atm



(burning rate 41 mm/s^{-1}) P-50 atm

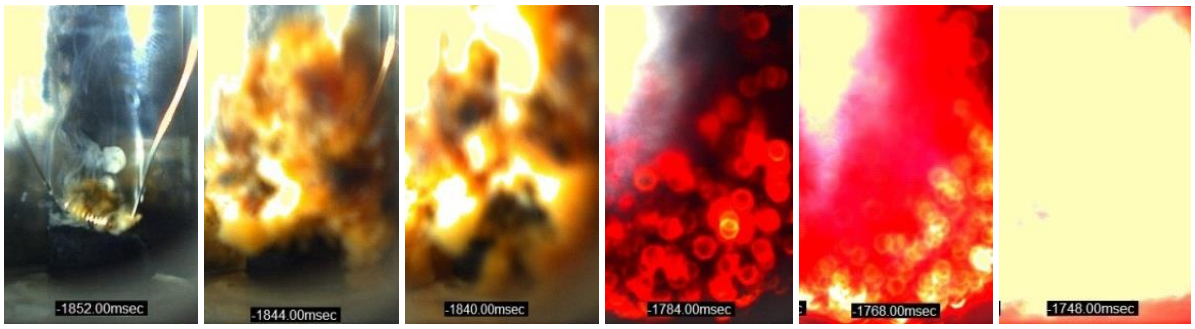
Fig. 3 - Pictures taken by high speed camera during combustion of 80% HAN-based propellant with 15% Carboxymethyl cellulose (CMC) and 5% CRH -475 at pressure of 10 atm., 30 atm. and 50 atm. in the strand burner

The results shows of the effect of carbonized rice husk on increasing of the burning rate of HAN / CMC composition at different pressures in compare with Fig 2. According to the oscilloscope

may be noted relatively positive acceleration of the burning rate of compositions at different pressures in the system pressure10 atm., 30 atm. and 50 atm. This equipment provides viewing the dynamics of combustion of the sample in a dynamic mode of initiation point until complete combustion.

The results shows of the effect of CRH-K_2CO_3-475 on increasing of the burning rate of HAN / CMC mixture at different pressures in compare with Fig 2. As seen in Figure 3, with the addition of activated carbon in the formulation at an initial pressure of 10 atm. burning rate is reached and take a place stable combustion with burning rate up to 11 mm/s^{-1}. The results shows the effect of increase of the burning rate after including CRH-K_2CO_3-475 in the HAN/CMC mixture at compared with Fig 2 results. Acceleration effect can be observed in all chosen points (10 atm., 30 atm. and 50 atm.) of initial pressure. Also, was to determine that the addition of CRH-K_2CO_3-475 in the mixture increases the concentration of the smoke at combustion test of samples. This is explained by the formation of carbon oxides CO and CO_2.

Figure 4 showsthat the dynamics of the combustion of CRH-K_2CO_3-475 without addition of CMC gel at 10 atm. initial pressure.



(burning rate 38 mm/s^{-1}) P-10atm

Fig. 4 - Pictures taken by high speed camera during combustion of 90% HAN-based propellant with 10% CRH -475 at pressure of 10 atm. and 50 atm. in the strand burner

When introduced into the carbonized rice husk combustion temperature rise observed for the thermocouple 191 ^oC to 330 ^oC. It should be noted that the burning of this system is stable and has a laminar flame, accompanied by a large amount of heat to form a solid combustion products. Characteristics of the above compositions show a good prospect of application of these combinations as propellants.

3.2 Experimental studies of decomposition HAN and carbonized rice husk

Thermal analysis by DTA-TG

Figure 5 shows the results of differential thermal analysis (DTA) and thermal gravimetric analysis (TG) at 20 K/min heating rate on Nitrogen media. The graph (a) shows data thermal decomposition HAN water solution (95%). Initial temperature point start from 185.2 ^oC. The graph (b) presents the thermal analysis of decomposition 90% HAN/10%CRH-K_2CO_3-475. After including activated carbon in the mixturethe initial temperature two times decries and held from 92.5 ^oC. Based on the DTA-TG results of the analysis in Figure 5 can assume the strong effect of CRH-K_2CO_3-475 on the decomposition of hydroxylammonium nitrate.

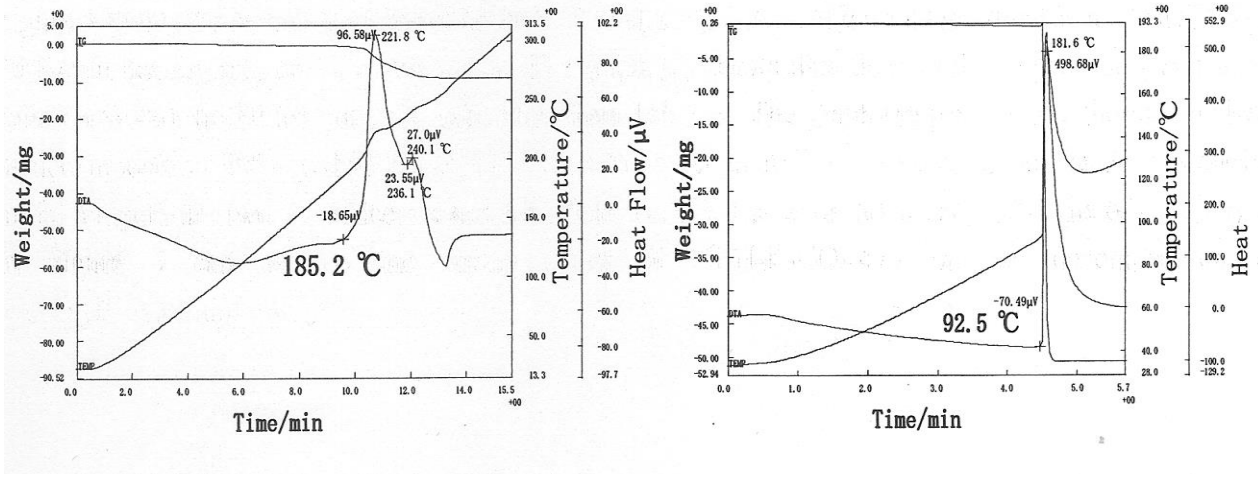
Based on DTA-TG results of thermal decomposition of HAN/CRH-K_2CO_3mixtures, were conducted experimental sets of decomposition analysis in different heating rate (5 K/min, 10 K/min, 15 K/min and 20 K/min). It is allowed us to calculated the activation energy by using the isoconversional method suggested by Starink [9,10], because this methods more accurate value. Results of calculations of activation energy by Ozawa plot 87,946 KJ/mol, by Kissenger a plot 83.835 KJ/mol compared with 112,968 KJ/mol [11]. Therefore possible to assume that the carbon exhibits pseudo catalytic effect of activated carbon.

Conclusion

- The results from the combustion process of HAN – based propellant and carbonized rice husk

additive showed an increase of burning rate, increasing the combustion temperature of 191 ° C up to 330 ° C. Experimental data indicate acceleration of burning rate at the addition up to 1% carbonized rice husk in the mixture.

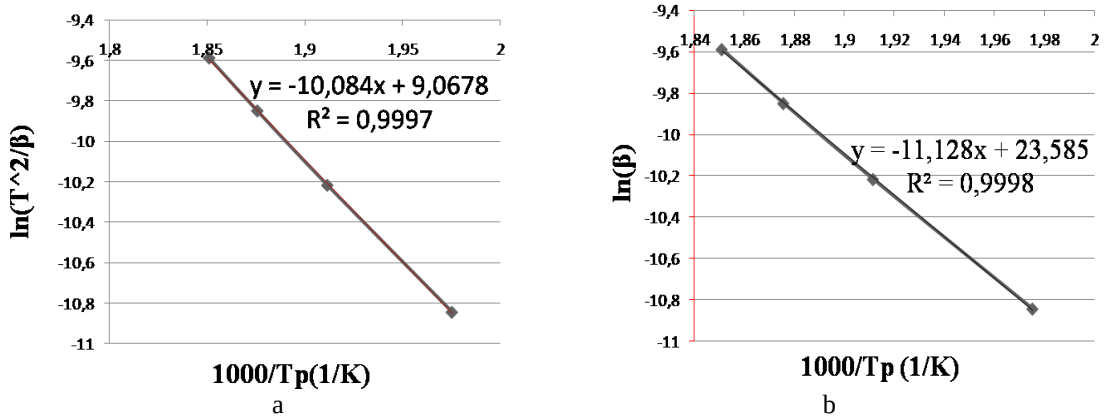
- Based on the results of experiments with carbonized rice husk included in HAN based mixture investigated by the TGA-DTA analysis, where one can observe lowering decomposition temperature of 185 ° C to 92 ° C, and decreasing of activation energy which could be describe as the pseudo catalytic reaction.



a b

a) DTA-TGA analysis of HAN decomposition (100%);
b) The DTA-TGA analysis HAN decomposition (90%) / CRH-475 (10%)

Fig. 5 - TGA-DTA results of the analysis at different ratios of HAN with CRH-475



a b

Fig. 6 - The non-isothermal analysis of activation energy of HAN based monopropellant with activated carbon by a) KISSINGER; b) OZAWA methods

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ГИДРОКСИЛАММОНИЙ НИТРАТЫН ДАЙЫНДАУ ЖӘНЕ КӨМІРТЕКТІ КҮРІШҚА УЫЗЫНКОСУ КЕЗІНДЕ ТЕРМИЯЛЫҚ ЫДЫРАУДЫ ЗЕРТТЕУ

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Аннотация
КөміртектікүрішқауызынанжасалғанK_2CO_3-белсендірілген көміртектіңкөмегімен 95%HAN отынының жанужылдамдығын арттыруы нәтижелері суреттелген. Зерттеу азот газы ортасында10, 30 и 50 атмосфера аралығындағы жоғары қысымдық камерасында өткізілді. Көміртекті күріш қауызы мен HAN отынның термиялық және каталитикалық ыдырау шығармаларын саралу үшін (ДТА) талдау және термогравиметриялық (ТГ) талдуы пайдалана отырып жүргізілді.Анализ алюминий тигельдерінде 100 мл/мин азот толқынында жүргізіп, зерттеулер 297K және 723K аралығындағы температурада бақыланды. Активтендірілген көмірді қосу кезіндеHAN жанарғысыңтұтану температурасың нүктесінің азайуы көрсетеді.ДТАнәтижелерін талдағаннан кейін активтендірілген көмірдіңHAN отынының ыдырауы Иридиң каталитикалық әсеріменсалыстырмалы ұқсастығы көрсеті
Түйінді сөздер: гидроксиламмонии нитраты, термиялық анализ, термогравиметриялық анализ, жылыту жылдамдығы

ПРИГОТОВЛЕНИЕ НИТРАТА ГИДРОКСИЛАММОНИЯ И ИССЛЕДОВАНИЕ ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ С КАРБОНИЗОВАННОЙ РИСОВОЙ ШЕЛУХОЙ

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Аннотация
Исследована скорость горения 95%-го раствора HAN с карбонизованной рисовой шелухой

активированной K_2CO_3. Исследования проводились в камере под высоким давлением в 10, 30 и 50 атмосфер в среде азота. Анализ термического и каталитического разложения составов HAN на основе ракетного топлива с карбонизованной рисовой шелухой были выполнены с помощью дифференциального термического (ДТА) и термогравиметрического анализа (ТГ). Исследования проведены при температурах в диапазоне от 297 К до 723К при потоке азота 100 мл/мин в алюминиевых тиглях. Результаты ДТА анализа показывают о снижения точки температуры воспламенения раствора HAN при добавлении активированного углерода, которые сравнительно близки с результатами каталитическим влияни иридия.

Ключевые слова: нитрат гидроксиламмония, термический анализ, термографический анализ, скорость горения