Experimental Investigations of Combustion Enhancement of HAN-based Green Propellant with K_2CO_3-Activated Carbon

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1 Abstract

The paper is focused on the effects of activated carbon with high specific surface area (SSA) based on vegetable raw materials as a carbonized rice husk (CRH-K_2CO_3) on the combustion performance of hydroxylammonium nitrate propellant (HAN: $[NH_3OH]^+[NO_3]^-$). The structure of activated carbon investigated by SEM, AFM and BET analysis. Were performed the combustion experiments to investigation of the influence of additives on the HAN linear burning rate. The kinetics study of HAN thermal decomposition with the activated carbon were assessed by differential thermal analysis (DTA – TG) at different heating rates. Based on DTA-TG results shown, that the additive of carbon decreases the ignition temperature of HAN on compared to the propellant alone. The carried out EI-MS analysis of the HAN propellant with activated carbon at different heating rates. It was shown the major products and product distribution of HAN decomposition with activated carbon.

2 Introduction

In the aerospace industry as liquid propellants in the satellite control elements mostly used hydrazine as a type of fuel. Unfortunately, propellants based on hydrazine considered extremely toxic [1]. HAN - is a high-energy substance that was the prospect of becoming a substitute for hydrazine, so it becomes very popular in the field of propellants [2]. 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. 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 [3-5].The problems of old and recent fuels is that they are performance still less satisfactory in use. Therefore, has been considerable interest in using additional additives like nanoparticles of Al and SiO_2 [6], variations of carbon or different catalysts to enhance of performance of propellants.
In this work, as the recent perspective additives investigated the carbonaceous material with high (SSA) activated carbon based on rice husk [7]. Rice husk is a large-scale vegetable unique material, e.g.: it is a renewable, green material with low commercial value [8].

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The paper consists of three main tasks: (i) Investigations of the carbonaceous material effect on the burning of HAN-based propellant in high-pressure. (ii) Kinetic analysis of the HAN decomposition supplied with SSA activated carbon by DTA-TG analysis. (iii) EI-MS analysis of combustion product distribution of HAN with activated carbon.

3 Experimental part

3.1 Burning test

The linear burning rate investigated in strand burner and high-pressure chamber, where placed the test samples and pressed by the nitrogen gas. The burning process recorded by Lab-view software (NI USB-6229) with the sampling rate of 1000 Hz and a high-speed camera PHOTRON, 250 fps, 640x488 pixels. The accuracy of pressure sensor is ±0.5% FSO - 0.076 MPa. The ignition carried out by electric power.

3.2 The differential thermal analysis

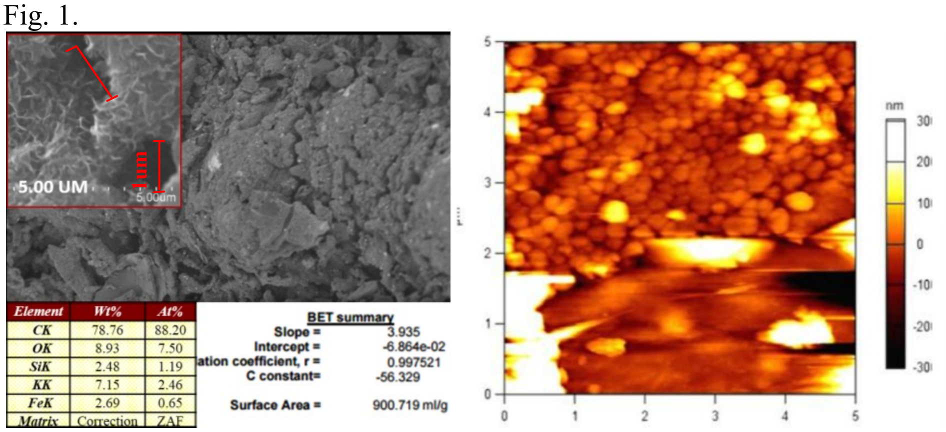
The HAN decompose was investigated by thermal analysis DTA-TG apparatus with a batch reactor. The dates recorded in the versus time, under nitrogen (100 ml min^{-1}) and different heating rates were fixed at 5-10 °C min^{-1}. In this study it was used a modulated DTA – TG apparatus operating at a temperature range between -180 and +725 °C and within ± 0.05 °C and a heating rate of 0.1 to 25 °C / m in with a sample weighing 200 mg.

3.3 Electron Ionization – Mass Spectrometry (EI-MS) analysis

The EI-MS analysis was investigated by using a TSQ 700 mass spectrometer with an adjustable heating rate of samples. The electron energy was 70 eV and the emission current was 200 mA. The ion source temperature was 150 °C, and the scan range was m=z 0-200. Trace amounts of test samples were loaded into aluminum crucibles and inserted directly into the source. The probe temperature was ramped from 25-600 °C at different heating rate 16K/min - 128 K/min.

4 Results and discussion

The characterization of morphology and elemental analysis of used a high (SSA) activated carbon CRH-K_2CO_3 shown in the scanning electron and atomic force microscope images, EDAX and BET analysis contained in Fig. 1.



Element	Wt%	At%
CK	78.76	88.20
OK	8.93	7.50
SiK	2.48	1.19
KK	7.15	2.46
FeK	2.69	0.65
Matrix	Correction	ZAF

a b

Figure 1. Scanning electron microscope image and BET analysis (a) and atomic-force microscopy (b) of morphology structure of CRH-K_2CO_3-475 activated carbon

On the presented images, are clearly visible the meso and macro pores and deepness of the used carbon which are approximately equal to 1-3 µm.

4.1 The combustion experiments in strand burner

The linear burning rates are determined using by two methods, first is break point based on breaking of strings from a combustion wave and second is determination of burning rate by graphical point relationship. To understanding of the effect of carbon was performed a comparative experiment of the HAN-based propellant combustion at 50 atm. illustrated in Fig. 2. In Figure 2 presented combustion tests of 95% HAN-based propellant with Carboxymethyl cellulose (CMC) (a) and Activated carbon CRH-K_2CO_3-475 (b) taken by high speed video camera. Based on taken video where shown the dynamics of combustion in Fig. 2 (a) possible to visual describe combustion of mixture at initial pressures at 50 atm. It should be noted that up to an initial pressure of 20 atm. ignition and burning of mixtures does not occur. At 20 atm. initial pressure observed that the samples start to boil and generated brown bubbles with generation of smoke, which indicates of the formation of NO_2 gas and further follows ignition with a bright front of flame with 4,73 mm/s^{-1} burning rate. At 50 atm. initial pressure burning rate reach up to 32.05 mm/s^{-1}.

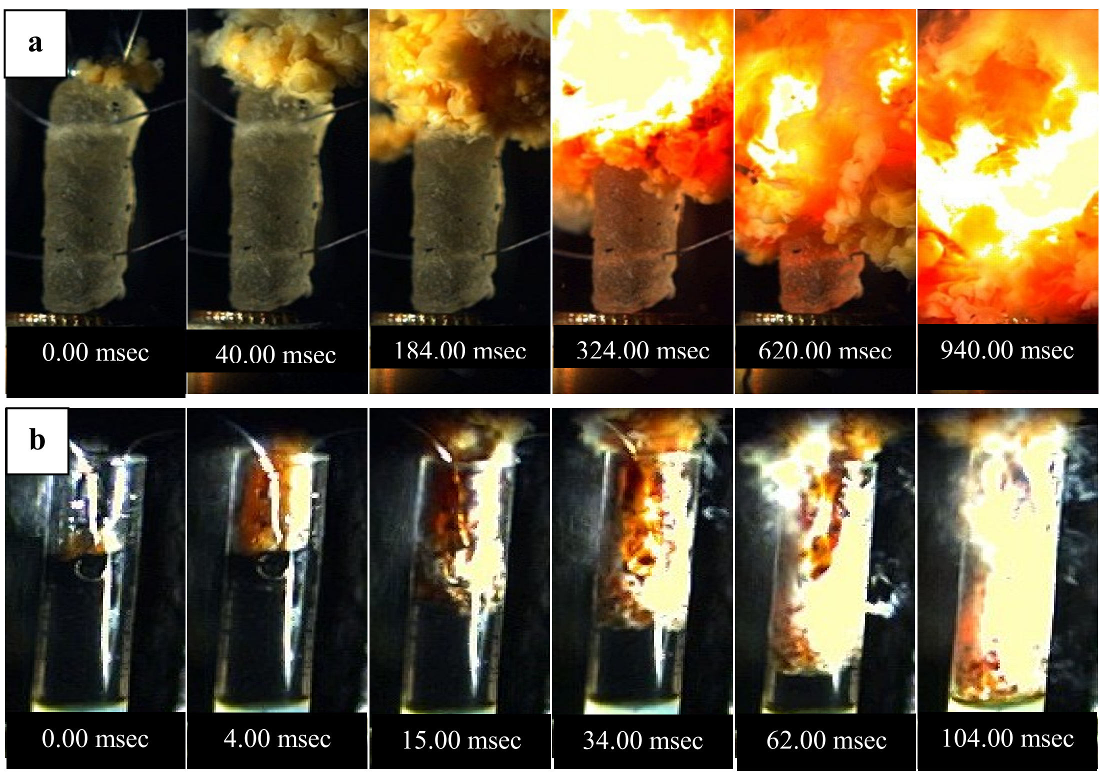


Figure 2. Captured images of regression process during combustion of HAN based propellant with various additives. (a) HAN-based propellant containing 10 wt % Carboxymethyl cellulose gel at 50 atm., r_b = 32.05 mm/s^{-1}. (b) HAN-based propellant containing 1 wt % Activated carbon (CRH-K_2CO_3) at 50 atm., r_b = 143.6 mm/s^{-1}.

As the results, the burning rate is much higher with the introduction of activated carbon. The high velocity achieved under equivalent initial pressure even the addition of the smallest additive 1% mass of using activated carbon. Note that the burning of both system with is stable and has a laminar flame, accompanied by the releasing of a large amount of heat and exhaust gases. The high burning rate of compositions with activated carbon is associated with a large active area and high carbon defectiveness. In the area of the structure defects occurs accumulation of energy as heat, which in turn increases the local temperature and the reaction rate. Characteristics of the above compositions show good prospect of application of these combinations as propellants.

4.2 Thermal analysis of HAN decomposition with activated carbon by DTA-TG

The kinetic analysis of HAN was assessed by DTA-TG. In the Fig. 3 shown the results of HAN decomposition at 20 K/min heating rate in N_2 media. The graph (a) shows thermal analysis of pure HAN, where initial temperature point start from 185.2 °C. The graph (b) presents the thermal analysis of decomposition 90% HAN with 10% CRH-K_2CO_3-475. In the samples, containing of the activated carbon, the initial temperature was decrease two times, until 92.5 °C. DTA-TG analysis results showed that the initial temperature of HAN decomposition in the presence of the obtained activated carbon is comparable to Iridium catalytic effect, e.g.: the effect of activated carbon 1 wt. on initial temperature from 185/86 °C vs 1% Iridium 185/75 °C.

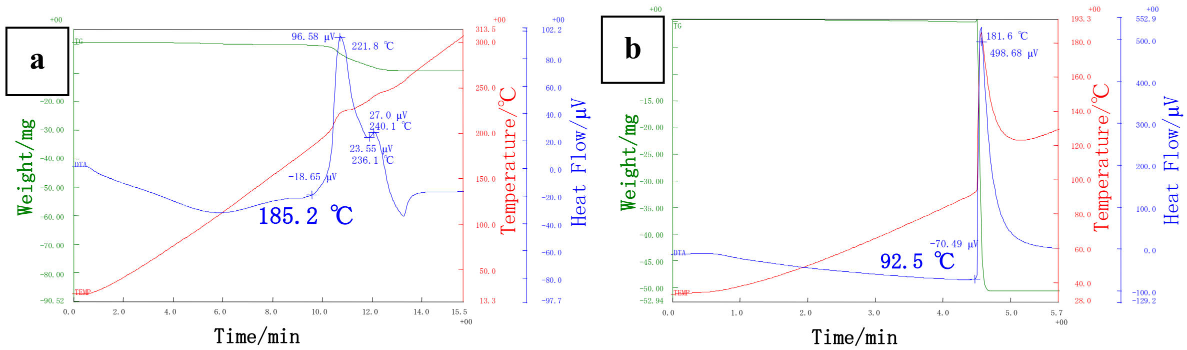


Figure 3. DTA-TG analysis results of HAN decomposition at 20 K/min heting rate
a) DTA-TG analysis of HAN-based propellant decomposition (100%); b) The DTA-TG analysis of HAN-based propellant containing 10 wt. % activated carbon (CRH-K_2CO_3)

4.3 The results of EI - MS

The mass spectrum analysis of HAN decomposition was investigated by EI-MS apparatuses. Based on the results is possible to identify of the product distribution of primary and secondary gaseous products. The mass spectrum of HAN decomposition with activated carbon (CRH-K_2CO_3) is shown in Fig. 4.

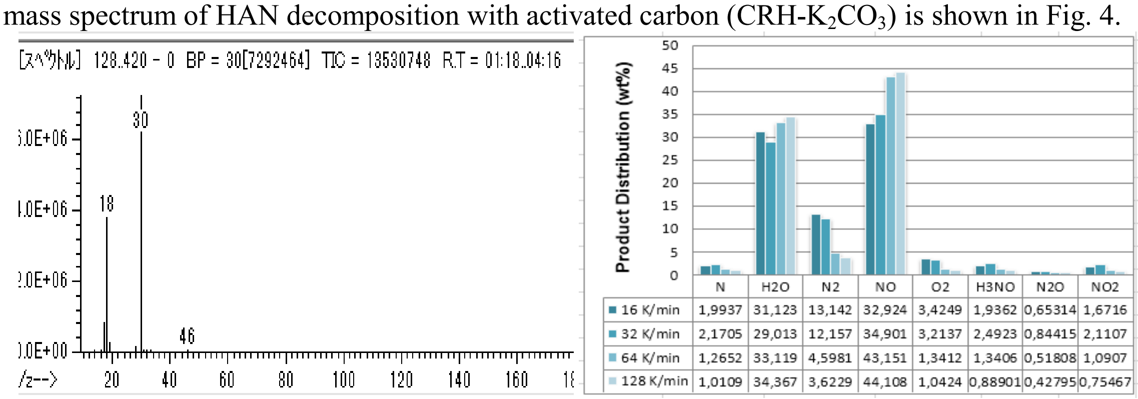


Figure 4. MS analysis of HAN decomposition with activated carbon CRH-475 K_2CO_3 and the product distribution at 64 K/min heating rate.

The ionization of mixture held on constant heating rate (64 K/min). The elemental composition of the most important fragment ions, determined by high resolution MS analysis, was the following: m/z 14 = N, m/z 18 = H_2O (major ion), m/z 28 = N_2, m/z 30 = NO (major ion), m/z 32 = O_2, m/z 33 = H_3NO (hydroxylamine), m/z 44 = N_2O, m/z 44 = NO_2. The results of the study completely coincide with the data of Lee, H., and Litzinger, T. A. work [10], where water, nitric acid and nitrogen oxides are the main products. The decomposition of HNO_3 is responsible for the formation of major gas products NO and NO_2. The formation rate of NO depends on the time of oxidation. The base decomposition products is water which always backed up by a peak m/z=17, m/z=18 and m/z=19, which indicates the water course. At low heating rate experiments around 16-32 K/min is defined that unrealized oxygen is responsible for the oxidation of NO to NO_2. This is can be seen clearly explained to a regular increase of NO_2 and decriseing of water at low speeds. Gas NO_2 rapidly dissociate at high pressures. When this process occurs and in formed products increases the concentration of NO_2 followed rapid decrease the reaction temperature due to consumption of heat for dissociation NO_2 molecules.

Conclusion

The linear burning rates of HAN based propellant have been studied at the high pressures, exploring the effects of activation carbon, based on vegetable raw materials. In all cases, the burning rate of HAN propellant was increased approximately three times with the addition of carbonaceous additives in comparison with used HAN/CMC mixture. The linear burning rate can be high even with low concentrations of activated carbon. Enhancement of the propellant burning rate is relate to the increasing heat of reaction, due to the accumulation of energy in the structural defects of carbon. The results from the combustion process of HAN – based propellant and carbonized rice husk additive showed that changed a mechanism of decomposition of reaction of pure HAN. The results EI-MS and DTA-TG shows acceleration of reaction rate, decreasing of ignition temperature, going down of activation energy and increasing of intensity of formation of gas products of propellant depend on type of injection carbon.

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