EFFECT OF KOH-ACTIVATED RICE HUSK ON THERMAL DECOMPOSITION OF HYDROXYLAMINE NITRATE MONOPROPELLANT

M.K. Atamanov[1*], Keiichi Hori[2], Rachid Amrousse[2], Z.A. Mansurov[1]
[1]Institute of Combustion Problems, Kazakhstan
[2]ISAS/JAXA, Japan

Abstract

The paper is focused on the effects of carbonaceous materials on the combustion performance of widely known rocket propellant hydroxylammonium nitrate (HAN: $[NH3OH]^+[NO3]^-$). In this work compared the combustion of the HAN-based propellant with that of carboxymethyl cellulose gel and high surface area activated carbon based on vegetable raw materials as a carbonized rice husk. Based on results described the influence of additives on the reaching of linear burning rates of the propellant, were determined under a range of pressures up 10 atm to 70 atm in nitrogen media as a pressurizing agent. A kinetics study of thermal decomposition of HAN propellant with the activated carbon activated carbon 1 wt. were assessed by differential thermal analysis (DTA – TG) at different heating rates. Based on DTA results shown, that the additives of activated carbon decreases the ignition temperature and activation energy of HAN propellant compared to the propellant alone. Carried out the hard ionization of the HAN and activated carbon mixture that investigated by electron ionization mass spectrometry at different heating rates (from 16 K/min to 128 K/min). The formation intensity of major products and product distribution showing the effect of activated carbon on thermal decomposition of HAN based propellant.

Keywords: *hydroxylammonium nitrate, activated carbon, burning rate, thermal analysis, EI-Mass spectroscopy*

1. Introduction

In the aerospace industry as liquid propellants in the satellite control elements, hydrazine mostly used as a type of fuel. Widely applicable catalyst for the monopropellants is iridium metal, which as known as very expensive. Unfortunately, propellants based on hydrazine considered extremely toxic. Among the possible alternatives of hydrazine use of ionic liquids containing ionic oxidizer, fuel and water as a new propellants [1, 2].

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 [3]. 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. 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 [4–6].

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 [8], variations of carbon or different catalysts to enhance of performance of rocket propellants.

In this work, as the recent perspective additives investigated the carbonaceous material with high specific surface area - Activated carbon (AC) based on rice husk (RH). RH is a large-scale vegetable unique material, e.g.: it is a renewable, green material with low commercial value [7].

The main purpose of research is the comprehensive study of combustion behavior of a "green alternative" propellant hydroxylamine nitrate in the presence of the different of high SSA (up to 3000 m^2/g) activated carbon types.

The paper consists of three main research tasks: (i) Experimental investigations of effect of carbonaceous material on the linear burning rates of the HAN-based propellant in high-pressure chamber. (ii) Kinetic analysis of the thermal decomposition of HAN-based propellant supplied with SSA activated carbon by DTA-TG analysis. (iii) EI-MS analysis of HAN thermal decomposition mixed with different types of activated carbon for understanding of effect of carbon on behavior of the investigated object.

2. Experimental

2.1 Burning test

To investigate the linear burning rate used strand burner and high-pressure chamber, the where test samples are placed and pressed by the nitrogen gas. The ignition delay, initial pressures and burning process recorded by Lab-view software (NI USB-6229) with the sampling rate of 1000 Hz. The accuracy of pressure sensor is ±0.5% FSO (Ful l Scale Output) which is equal to 0.076 MPa. The high-pressure chamber equipped with a high-speed camera PHOTRON with the settings 250 frames per second and a resolution of 640h488 pixels. The full experimental setup shown in *Fig. 1*. The experiments of combustion of HAN monopropellant with carbonized rice husk was carried out in high-pressure chamber by ignition with electric power at constant pressures from 10 atm up to 70 atm. 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 embedded with sensors for determining of burning rate by method of break point [1], which connected to the oscilloscope. Upon reaching the required level of pressure initiation performed by external electric power and a polymer binder GAP (glycidyl azide polymer).

2.2 The differential thermal analysis

The thermal and catalytic decompose of HAN-based propellant in the presence of the activated carbon investigated by thermal analysis apparatus with a batch reactor. Thermal analysis combines several methods of investigation after a TGA, DTA methods TG-DSC. The DTA-TG dates recorded in the versus time, under nitrogen/argon flow (100 ml min^{-1}) and heating rates were fixed at 5-10°C min^{-1} for thermal decomposition and 1°C min^{-1} for catalytic degradation.

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 / min with a sample weighing 200 mg. The this case DTA-TG allows to able to obtain the following information: (a) initial temperatures; (b) evaporation point (endothermic peak); (c) temperature of decomposition given by the inflexion point of the temperature curve; d) mass loss etc [9].

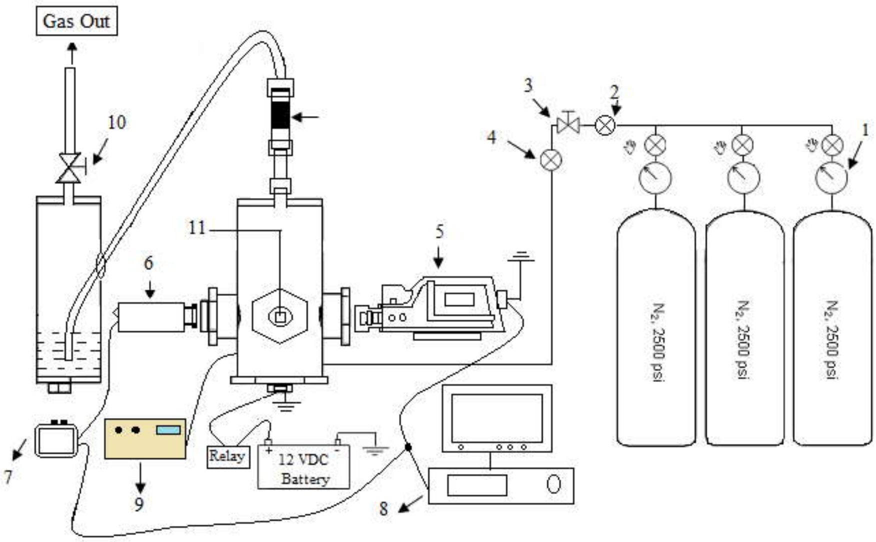


Fig. 1. Scheme of an enclosed bomb to testing of burning rate

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

The EI spectra 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 ^{o}C, and the scan range was m=z 0-200. Trace amounts of test samples were loaded into aluminum crucibles (SUS) and inserted directly into the source. The probe temperature was ramped from 25 C to 600 ^{o}C at different heating rate 16K/min, 32 K/min, 64 K/min and 128 K/min. Data acquisition was start immediately following insertion.

3. Results and discussion

3.1 The combustion experiments in strand burner

Different types of high SSA activated carbon additives have been investigated and their effects on propellant and enhance of the performance characteristics was analyzed. The linear burning rates of the HAN-based propellant with the activated carbon additives monitored and recorded by high-speed camera. In the results shown the ignition and burning characterization as a function of additive concentration and initial pressure. 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. In the Fig. 2. shown compare the combustion of: (a) HAN-based propellant with that of carboxymethyl cellulose gel; (b) HAN-based propellant with that of carboxymethyl cellulose gel and high surface area activated carbon; (c) HAN-based propellant with activated carbon without gel (*lq*) at 50 atm pressure.

As the results, can be seen that burn rate is much improved 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. Noted, 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. Characteristics of the above compositions show a good prospect of application of these combinations as propellants.

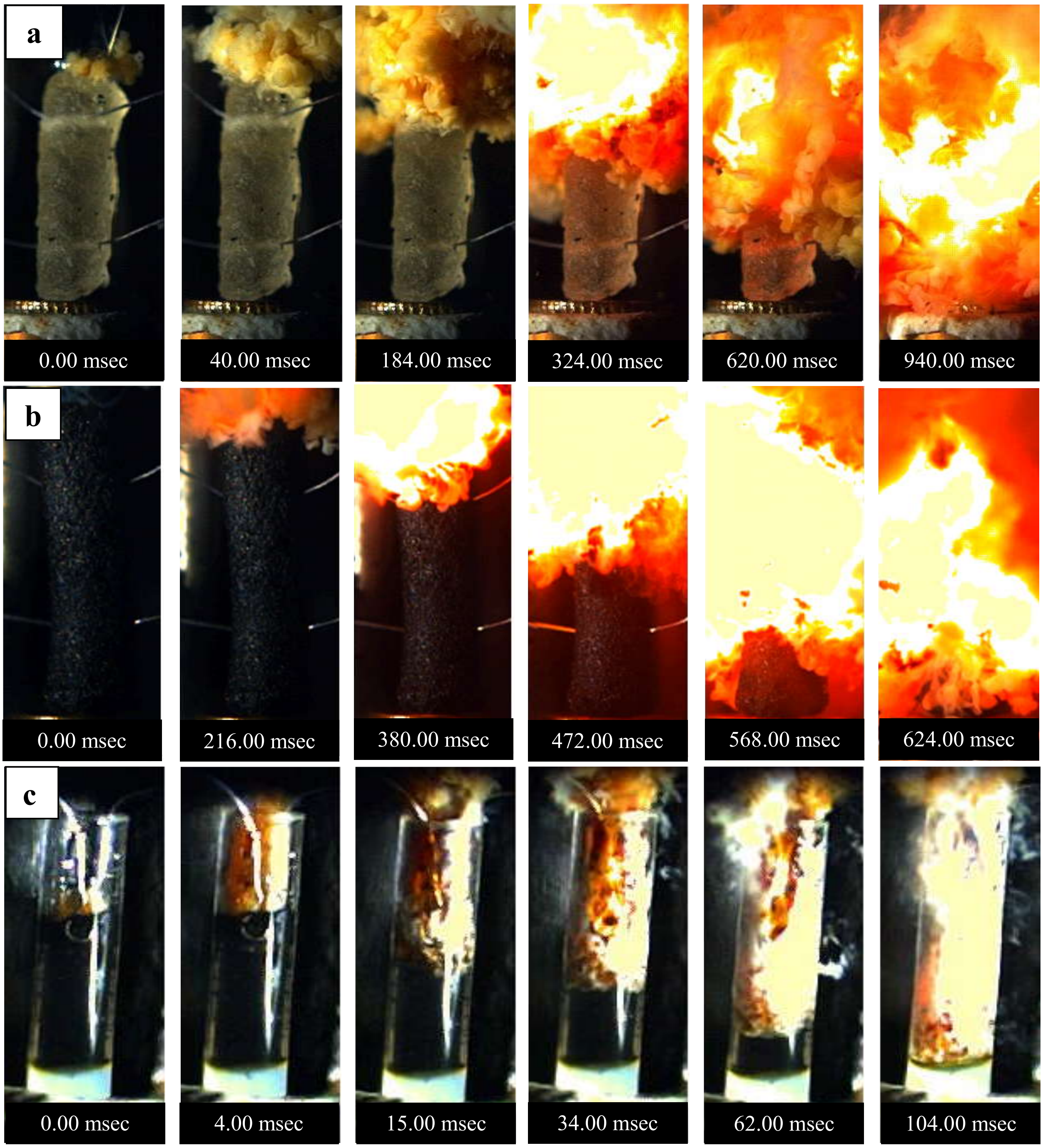


Fig. 2. Captured images of regression process during combustion of HAN based propellant with various additives.

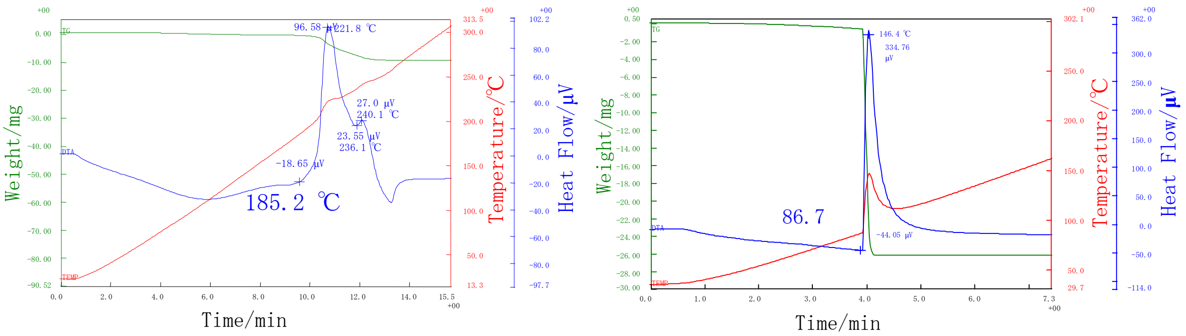
(a) HAN-based propellant containing 10 wt % Carboxymethyl cellulose gel at 50 atm., r_b = 32.05 mm/s^{-1}.

(b) HAN-based propellant containing 10 wt % Carboxymethyl cellulose gel and 1 wt % Activated carbon (CRH-KOH) at 50 atm., r_b = 52.9 mm/s^{-1}.

(c) HAN-based propellant containing 1 wt % Activated carbon (CRH-KOH) at 50 atm., r_b = 143.6 mm/s^{-1}.

3.2 Experimental studies of Thermal analysis of decomposition HAN with carbonized rice husk by DTA-TG

Figure 3 shows the results of DTA and TGA at 20 K/min heating rate on nitrogen media. The graph (a) shows data thermal decomposition HAN water solution (95%) where initial temperature point start from 185.2 °C. The graph (b) presents the thermal analysis of decomposition 90% HAN with 10% CRH-KOH-475. After including activated carbon in the mixture the initial temperature two times decries and held from 86 °C.



a **b**

Fig. 3. TGA-DTA results of the analysis at different ratios of HAN with CRH-KOH: a) DTA-TGA analysis of HAN decomposition (100%); b) The DTA-TGA analysis HAN decomposition (90%) / CRH-KOH (10%);

Decomposition kinetics of mixture (HAN spiked with the 1 AC mass %) was assessed by DTA – TG thermal analysis at different heating rates. 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, e.g.: the effect of 1% AC on initial temperature from 185/86 °C vs 1% Ir 185/75 °C. The thermal decomposition of HAN/CRH-KOH mixtures, were conducted experimental sets of decomposition analysis in different heating rate (5 K/min, 10 K/min, 15 K/min and 20 K/min). Based on the DTA-TG results of the analysis in Figure 1 can assume the strong effect of CRH- KOH -475 on the decomposition of hydroxylammonium nitrate. Study the decomposition at different heating rates is allowed (in Figure 4) us to calculated the activation energy by using the isoconversional method suggested by Starink [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. Therefore possible to assume that the carbon exhibits pseudo catalytic effect of activated carbon.

a **b**

Fig. 4. The non-isothermal analysis of activation energy of HAN based monopropellant with activated carbon by a) KISSINGER; b) OZAWA methods.

3.1 The results of EI - MS

Presented the results of mass spectrum of a HAN based propellant with carbonaceous materials. Effect of the heating rate on product distribution of HAN based propellant with addition of different types of activated carbon (CRH-KOH and CRH- K_2CO_3). Shown the comparison of the product distribution of primary and secondary gaseous products during the decomposition of investigated materials. The mass spectrum of a HAN based propellant with activated carbon (CRH-KOH) is shown in Figure 5. The hard ionization analysis held on 64 K/min heating rate conditions by EI - MS. The observed spectra at the initial temperature and total ion current intensities increased with temperature around 450 °C. The base peak, m/z=30 (NO), which proves that the peaks m/z=46 (NO_2). Peak m/z=28) corresponds to a molecule of CO gas that is formed through the interaction of activated carbon KOH-activated with hydroxylamine nitrate.

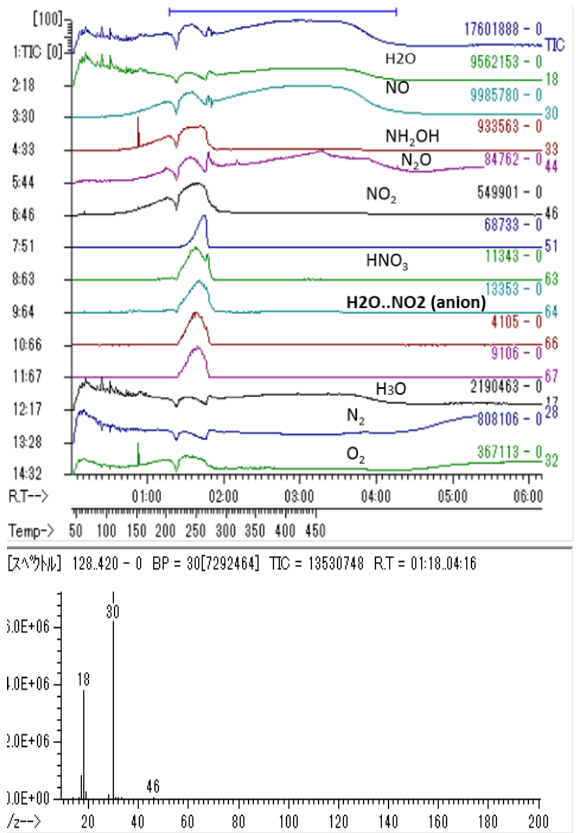
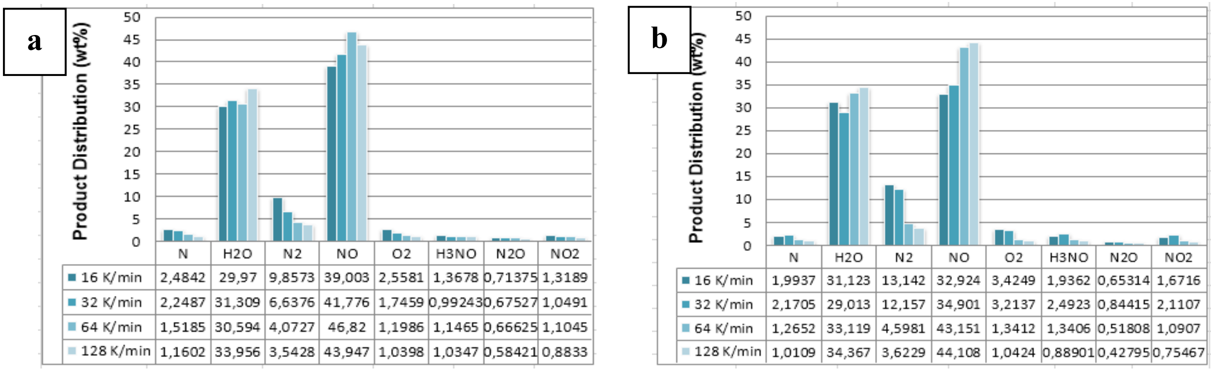


Fig. 5. EI-MS analysis of total gaseous products of decomposition of HAN with carbonized

rice husk.

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 [11], where water, nitric acid and nitrogen oxides are the main products.

Figure 6 shows the EI-MS analysis of HAN at different heating rates. Impact of heating rate on HAN mixture moiety affect on the change of products distribution of two important ions, m/z 30 and ion m/z 46. Distribution of the products of major gases (NO, NO_2 and H_2O) was varied. The obtained major gas products of the decomposition of HNO_3 is responsible for the formation of NO and NO_2. The formation rate of nitrogen oxide depends on the time of oxidation. Shown all detected formation products of formulation decomposition. Peak 33 m/z indicate the formation of H_3NO. It should be noted that the substance is always backed up by a peak 16 m/z and 32 m/z peaks (oxygen) and 17 m/z, 18 m/z 19 and m/z, which indicates the water course.



(a)	N	H2O	N2	NO	O2	H3NO	N2O	NO2
16 K/min	2,4842	29,97	9,8573	39,003	2,5581	1,3678	0,71375	1,3189
32 K/min	2,2487	31,309	6,6376	41,776	1,7459	0,99243	0,67527	1,0491
64 K/min	1,5185	30,594	4,0727	46,82	1,1986	1,1465	0,66625	1,1045
128 K/min	1,1602	33,956	3,5428	43,947	1,0398	1,0347	0,58421	0,8833

(b)	N	H2O	N2	NO	O2	H3NO	N2O	NO2
16 K/min	1,9937	31,123	13,142	32,924	3,4249	1,9362	0,65314	1,6716
32 K/min	2,1705	29,013	12,157	34,901	3,2137	2,4923	0,84415	2,1107
64 K/min	1,2652	33,119	4,5981	43,151	1,3412	1,3406	0,51808	1,0907
128 K/min	1,0109	34,367	3,6229	44,108	1,0424	0,88901	0,42795	0,75467

Fig. 6. Effect of heating rate on the product distribution of HAN decomposition with a) CRH-KOH; b) CRH-475 K_2CO_3 at 64 K/min heating rate.

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 intensity 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.

The including of activated carbon in the propellant composition, the m/z 30 = NO concentration is clearly decreases. It is shown that in order to reduce the pollution of NO gas, the type of used carbon acts an important role. The comparison of the products distribution depend on type of AC shown in Fig. 7. When carbon is added, the formation of NO gas falling down to 25-30%, which is a fairly interesting effect, considering the activated carbon concentration of only 1% of the total mass.

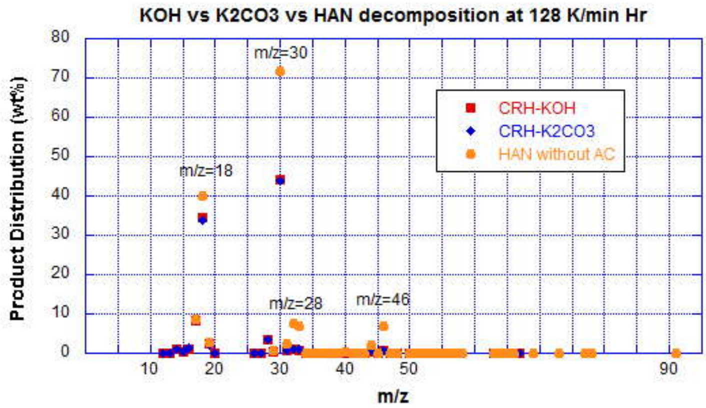


Fig. 7. Comparison of product ion distribution for KOH and K_2CO_3 activated carbon and pure HAN without carbon at 128 K/min heating rate

Conclusion

The linear burning rates of HAN based propellant have been studied at the high pressures, exploring the effects of carbonaceous materials additives, based on vegetable raw materials as a carbonized rice husk. In all cases, the burning rate of HAN propellant was increased approximately tree times with the addition of carbonaceous additives in comparison with used HAN/CMC mixture. Also, shown that the linear burning rate of HAN can be high that other additives, 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.

References

[1] Rachid Amrousse, Toyoshiyuki Katsumi, Noboru Itouyama, Nobuyuki Azuma, Hideshi Kagawa, Keigo Hatai, Hirohide Ikeda, Keiichi Hori, New HAN based mixtures for reaction control system and low toxic spacecraft ppropoulsion subsystem: Termal decomposition and possible thruster applications // Combustion and flame 162 (2015) 2686-2692

[2] R. Amrousse, K. Hori, W. Fetimi, K. Farhat, HAN and ADN as liquid ionic monopropellants: Thermal and catalytic decomposition processes, Appl. Catal. B 127 (2012) 121–128.

[3]W.F. Oberle, G.P. Wren, Closed chamber combustion rates of liquid propellant in 1846 conditioned ambient, hot and cold vulnerability testing of liquid propellant LGP 1846, Proceedings of 27th JANNAF Combustion Subcommittee Meeting, vol. 557, CPIA Publication, Huntsville, 1990, pp. 377-385.

[4] W.F. Oberle, G.P. Wren, Burn rates of LGP 1846 conditioned ambient, hot, and cold, ballistic research laboratory technical report no. BRL-TR-3287, 1991.

[5] S.T. Jennings, Y. Chang, D. Koch, K.K. Kuo, Peculiar combustion characteristics of XM46 liquid propellant, in: Proceedings of 34th JANNAF combustion subcommittee meeting, vol. 662, 1997, pp 321-331

[6] Justin L. Sabourin, Daniel M. Dabbs, Richard A. Yetter, Frederick L. Dryer and Ilhan A. Aksay, Functionalized Graphene Sheet Colloids for Enhanced Fuel/Propellant Combustion // ACS Nano, 2009, 3 (12), pp 3945–3954

[7] Azat S., Pavlenko V.V, Kerimkulova A.R., Mansurov Z.A. Synthesis and structure determination of carbonized nano mesoporous materials based on vegetable raw materials. Advanced Materials Research Vols. 535-537 (2012).

[8] Atamanov M.K. Tomioshi Sh. Z.A. Mansurov The process of combustion and thermal analysis system of ammonium nitrate and carbonized rice husk // Proceedings of the VIII International Symposium "burning and plasma chemistry" and scientific-technical conference "Energy Efficiency 2015", September 16-18, 2015, Almaty, Kazakhstan - S. 243- 245.
[9] Barzykin Thermal analysis of the reactants // Combustion and Plasma Chemistry, 2004, Volume 2, №4, s.275-292
[10] Starink, M. J. The determination of activation energy from linear heating rate experiments:. *Thermochimica Acta,* **404**, 2003, pp. 163-176.
[11] Lee, H., and Litzinger, T. A., "Thermal decomposition of HAN–based liquid propellants," Combustion and Flame, Vol. 127, Issue 4, 2001, pp. 2205-2222.