

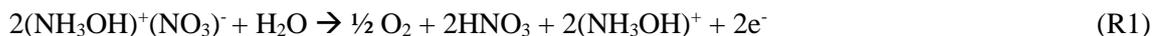
# Characterization of High Pressure Electrolytic Decomposition of Hydroxylammonium Nitrate Aqueous Solution using FTIR

Kuan-Io Lao, Yu-Ting Chou, Ming-Hsun Wu\*  
Department of Mechanical Engineering, National Cheng Kung University  
Tainan City, Taiwan

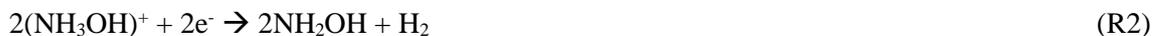
## 1 Introduction

Hydroxylammonium nitrate (HAN), an energetic ionic liquid, is considered as a potential substitute of hydrazine, a highly toxic propellant. NASA has chosen AF-M315E, a HAN-based propellant as the new monopropellant for the Green Propellant Infusion Mission (GPIM) [1]. Electrolytic and catalytic decomposition of HAN are both feasible ignition approaches for the ionic liquid. When ignited by electrolytic approach, ignition could occur under room temperature. The gas products of electrolysis (hydrogen generated at the cathode and oxygen generated at the anode) could help reaching self-sustained combustion afterwards, and the reaction rate is proportional to the voltage applied [2,3]. The ignition delay and current applied show a relation of power function [4]. HAN would undergo electrolysis in the presence of water [5]. The reaction equations are stated below [6].

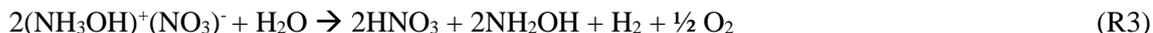
At anode:



At cathode:



Global reaction:



Apparently, the catalytic decomposition is well-proven in propulsion industry and relatively better understood, whilst the electrolytic mechanism needs further investigation. Being a pressure-sensitive solution, HAN needs to be tested under different pressure to characterize the pressure dependence.

In this work, a series of HAN electrolysis experiments were conducted under various initial pressures. Temperature and pressure inside the batch reactor were recorded for further analysis. Synchronized data illustrating the reaction profile were monitored by Fourier Transform Infrared Spectrometer (FTIR) during each reaction.

## 2 Experimental Method

### Materials

Hydroxylammonium nitrate (HAN) aqueous solution of 76% by weight was used for all tests in the present work. It was prepared in-house by titration of hydroxylamine ( $\text{NH}_2\text{OH}$ ) and nitric acid ( $\text{HNO}_3$ ) under a low temperature bath. The HAN aqueous solution formed was in a low concentration of about 25 wt.%. It was then concentrated using rotary evaporator to approximately 92 wt.% and diluted to 76 wt.% for the present work.

### Apparatus and Procedures

A custom-made high-pressure batch reactor (shown in Fig. 1a), which could stand up to 80 bar, was used in this work. An alumina crucible was placed at the bottom of the batch reactor (shown as Fig. 1b). Two titanium electrodes were fixed on a support attached to the lid of the reactor (shown as Fig. 1c). A heater was positioned under the crucible, it was set to be  $40^\circ\text{C}$  throughout the whole reaction. Two K-type (SCAXL-032U-12, Omega Engineering) thermocouples were inserted into the reactor, one with its tip touching the bottom of the crucible, to measure the temperature of the sample ( $T_{\text{bot}}$ ), while the other was hung that its tip located just above the crucible, as to measure the temperature of the gas phase ( $T_{\text{top}}$ ).

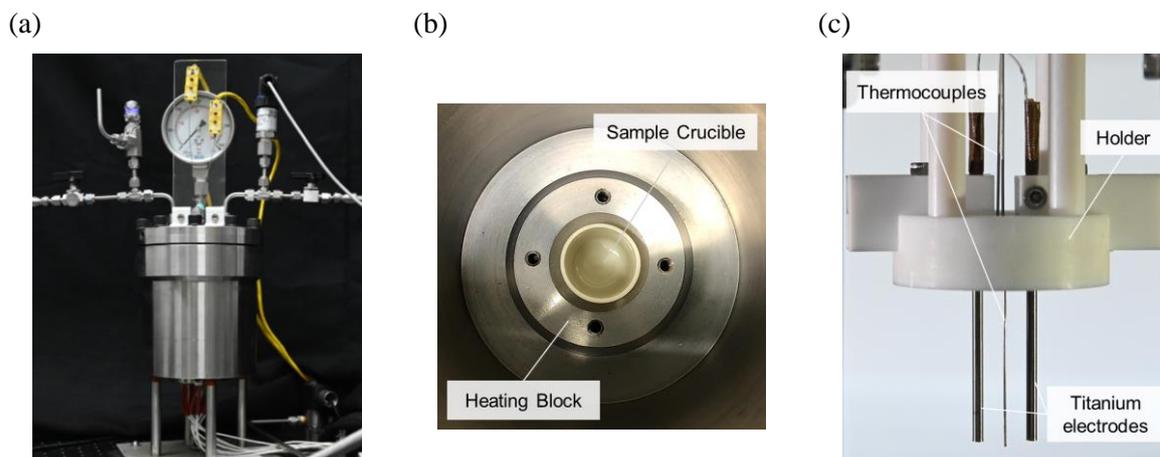


Figure 1: (a) Exterior view of the high-pressure batch reactor, (b) Top view of the sample crucible sitting in cavity of the heating block inside the reactor, and (c) The support of electrodes inside the reactor

The initial pressure of the high-pressure batch reactor was set to be 6, 11 and 21 bar (absolute pressure). Argon served as background gas in this work to prevent the formation of undesired by-products of reaction between HAN and air. A back pressure regulator was installed to keep the pressure inside the reactor steady. The pressure inside the reactor, temperatures of the heater, sample and gas phase above the crucible were recorded using a multi-channel data acquisition system (cDAQ 9189, National Instruments) for further analysis.

In each set of experiment, 2.0 ml (approximately 3.0 g) of 76 wt.% HAN aqueous solution was placed inside the crucible, then set in the middle bottom of the reactor. A voltage of 60 volt and current of 5 amp were applied for 5 seconds [7]. Gas generated by electrolysis was analyzed using FTIR (Tensor 27, Bruker) during the reaction process to illustrate the reaction profile. Nitrogen oxides including NO,  $\text{NO}_2$  and  $\text{N}_2\text{O}$  were identified using FTIR.

Figure 2 outlines the sampling flow network of this work. The decomposition of HAN aqueous solution would be carried out in the reactor. The gaseous products generated during the reaction will pass through the back pressure regulator, then be examined by FTIR. A spectrum illustrating the gas composition is

formed every 6 seconds (4 scans). The reaction profile composed of these spectra are displayed below (see Fig. 4). After reaction, the gas in the reactor would be collected into a sampling bag for the further analysis. After sampling, the electromagnetic valve would be opened to allow purging and cooling of the reactor.

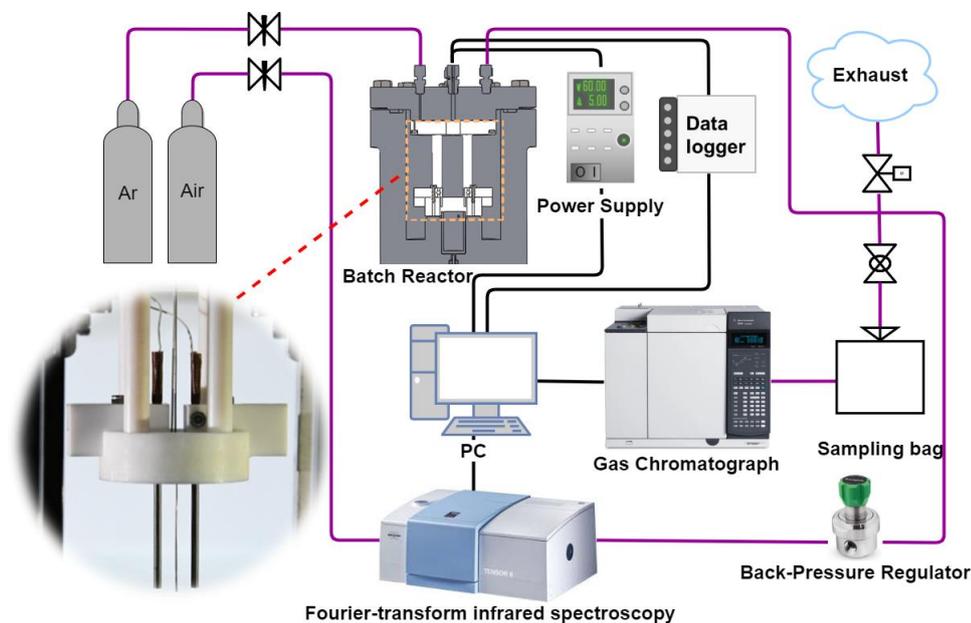


Figure 2: Sampling flow network.

As mentioned above, two thermocouples were installed in the reactor. The temperature of HAN solution sample ( $T_{\text{bot}}$ ) was recorded by the one with its tip touching the bottom of the crucible, while the other thermocouple was managed to measure the temperature of the gas phase above the sample holder ( $T_{\text{top}}$ ). Several parameters were derived from these data to characterize the decomposition performance. The decomposition onset temperature ( $T_{\text{dec}}$ ) was defined as the value of  $T_{\text{bot}}$  when  $dT_{\text{bot}}/dt$  exceeded 10. When more than one exothermic peak existed, the greatest one was considered to obtain the data of  $T_{\text{dec}}$ .  $T_{\text{max}}$  was literally the maximum recording of  $T_{\text{bot}}$  during the reaction.  $\Delta T$  was simply the difference between  $T_{\text{max}}$  and  $T_{\text{dec}}$ , it indicates the amount of heat generated. Temperature increase rate,  $S_p$ , is defined as the ratio of  $\Delta T$  and the time duration for temperature to increase from  $T_{\text{dec}}$  to  $T_{\text{max}}$ . The time of ignition delay is defined as the time needed for  $T_{\text{dec}}$  to reach  $T_{\text{max}}$ .

### 3 Result and Discussion

Figure 3a illustrates the evolution of temperature and pressure of each reaction. Voltage and current were applied at the 5<sup>th</sup> sec, such that the period of 5 to 10 sec was the duration of electrolysis. Two-stage reaction was observed under an initial pressure of 6 bar as a minor exothermic peak was observed. In the major exothermic peak, the  $T_{\text{bot}}$  increased from 50°C to 156.3°C with a temperature ramp rate of 18.2 °C/sec. Yet, only one exothermic peak was observed for initial pressure of 11 and 21 bar. For the condition under 11 bar, the  $T_{\text{bot}}$  reached a maximum of 171.1°C with a temperature increase rate of 24 °C/sec. It is noteworthy that the temperature ramp rate under initial pressure of 21 bar was precipitous, which was recorded to be 518.2 °C/sec. In other words, the  $T_{\text{bot}}$  climbed to its maximum almost instantaneously when the voltage was applied. The time of ignition delay for initial pressure of 6, 11 and 21 bar were 7, 5.25 and 0.25 sec (0.25 sec is the minimum time resolution of the measurements) respectively. The ignition delay is dependent to the pressure apparently.

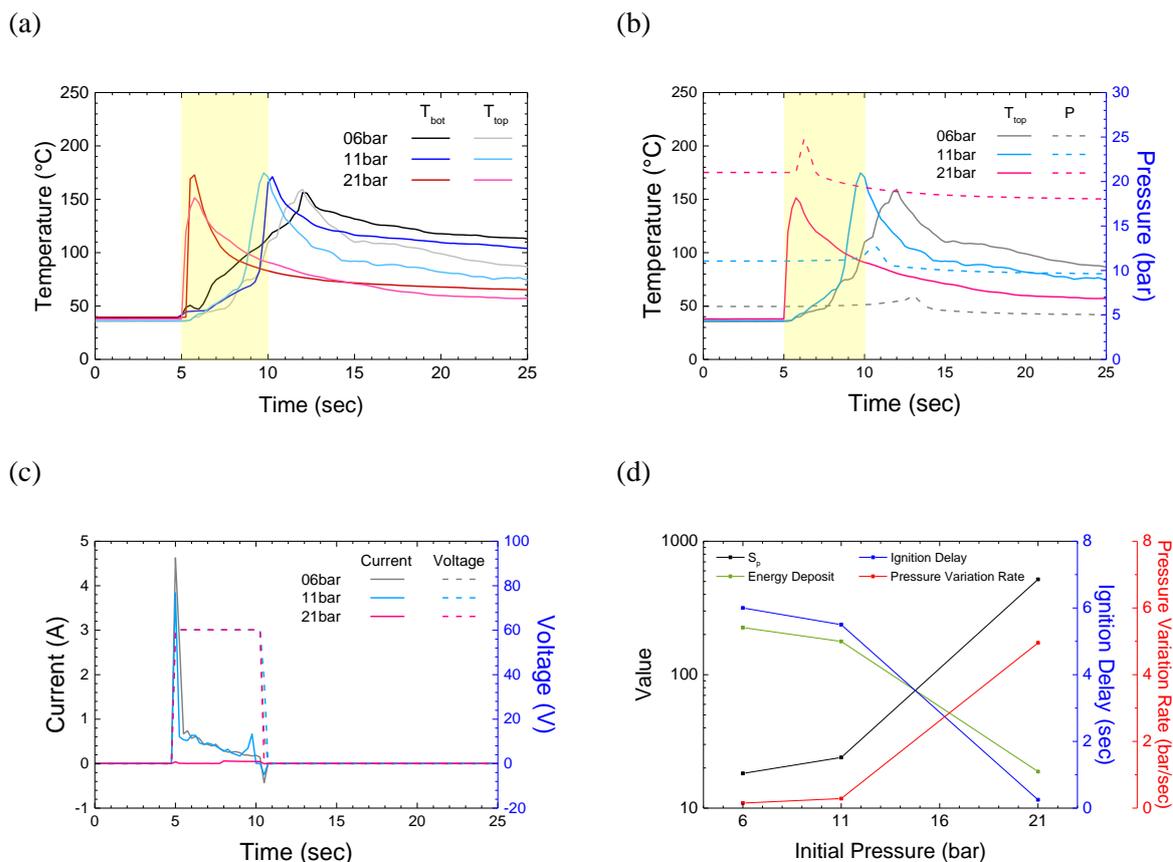


Figure 3: (a) Temperature evolutions under various initial pressures, (b)  $T_{top}$  and pressure evolution under various initial pressures, (c) Voltage and Current vs. time under various initial pressure, and (d) Temperature increase rate, energy deposit, ignition delay and pressure variation rate vs. pressure. The shaded regions represent the duration of electrolysis.

Under initial pressure of 6 bar, the  $T_{bot}$  continued to increase even after the electrolysis was over and reached a peak of 156.3°C at the 12<sup>th</sup> sec. This is considered as self-sustained reaction. And only under the initial pressure of 6 bar, did the HAN inside the crucible was all reacted. In the cases of initial pressure 11 and 21 bar, there was a little residual observed after reaction. Although a back pressure valve was installed in the reaction flow network, the pressure recorded still showed a small spike when pressure inside the reactor increased abruptly, as illustrated in Fig. 3b. The changes in pressure followed right after the changes in  $T_{top}$ . Figure 3c shows the voltage and current recorded during the reactions. As mentioned before, voltage of 60 volt and current of 5 amp were applied from 5<sup>th</sup> to 10<sup>th</sup> sec. The voltage readings were almost identical. However, the current readings of the reaction under initial pressure of 21 bar was different from that of 6 and 11 bar. The current readings were so low that almost no current was detected. This deduced that the reaction under 21 bar was so vigorous that gas bubbles were formed right after ignition, this greatly increased the resistance and lowered the current. Figure 3d illustrates the temperature increase rate ( $S_p$ ), energy deposit, ignition delay and pressure variation rate under several initial pressures. As HAN is highly sensitive to pressure, the parameters alter under different pressures. The  $S_p$  and energy deposit tend to rise against pressure, while the ignition delay and pressure variation rate increase with pressure.

Synchronized time-resolved FTIR measurement was carried out and illustrated in Fig. 4 below. The spectra with greatest absorbance were selected and displayed beside. The major products of HAN electrolysis are  $H_2O$ ,  $NO$ ,  $NO_2$  and  $N_2O$  [8, 9]. By the graph, it was clear that the reaction under different

pressure gave out products of the same species, yet different intensity. Further refinements on the sampling resolution and quantification of the spectra were necessary to better interpret the results.

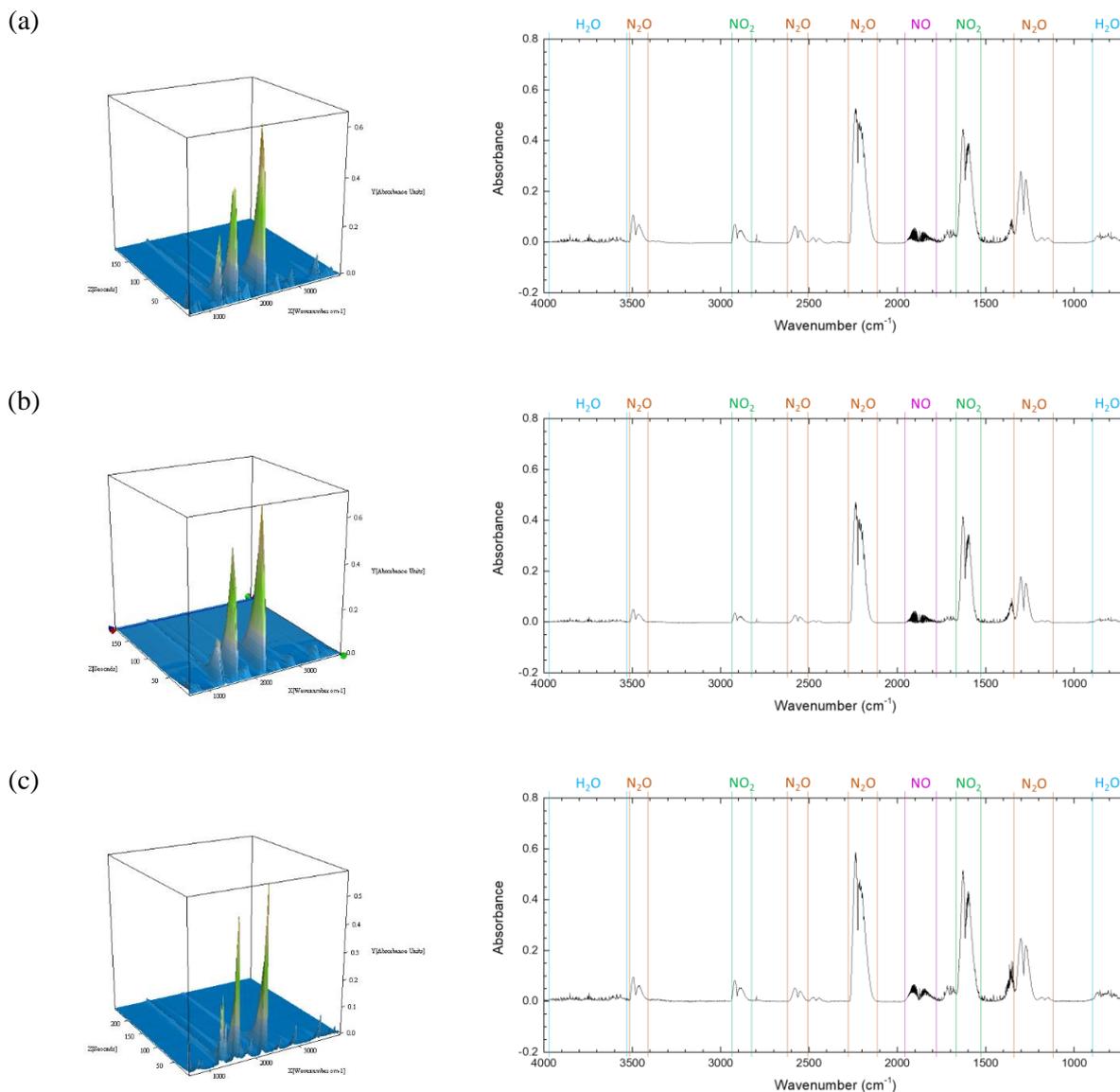


Figure 4: FTIR spectra of the reaction profile and the specific spectrum at peak with initial pressure of (a) 6bar, (b) 11bar and (c) 21bar.

## 4 Conclusions

Electrolytic ignition of HAN aqueous solution is feasible that decomposition of HAN can be triggered when 60 volt was applied. Meanwhile, HAN is very sensitive to pressure that the initial conditions with the same applied voltage and current, but different pressure would lead to different reaction profiles. Greater pressure brings a shorter ignition delay and higher maximum temperature that under initial pressure of 21 bar, the reaction was triggered almost immediately. The FTIR spectra tell that the reaction

path under different initial pressure might differ, tend to bring out the same major products with different composition.

## 5 Acknowledgment

This work is supported by the Ministry of Science and Technology, under grants MOST 110-2221-E006-091-MY2 and National Space Organization, Taiwan.

## References

- [1] Masse R, Spores RA, Kimbrel S, Allen M, Lorimor E, Myers P, McLean C. (2015). GPIM AF-M315E propulsion system. Prop and Ener Forum.
- [2] Meng H, Khare P, Risha G, Yetter RA, Yang V. (2009). Decomposition and ignition of HAN-based monopropellants by Electrolysis, AIAA 451.
- [3] Chai WS, Cheah KH, Koh KS, Chin JK. (2016). Parametric studies of electrolytic decomposition of hydroxylammonium nitrate (HAN) energetic ionic liquid in microreactor using image processing technique, Chemical engineering journal 296.
- [4] Khare P, Yang V, Meng H, Yetter RA. (2015). Thermal and electrolytic decomposition and ignition of HAN-water solutions, Combust. Sci. Technol. 187.
- [5] Wu MH, Yetter RA. (2019). A novel electrolytic ignition monopropellant microthruster based on low temperature co-fired ceramic tape technology. Lap Chip 9: 7.
- [6] Kuo BH. (2010). A study on the electrolytic decomposition of HAN-based propellants for microthruster applications. A master's thesis in Mechanical Engineering, The Pennsylvania State University.
- [7] OuYang H. (2020). Synthesis and atmospheric electrolytic decomposition characteristics of hydroxylammonia nitrate aqueous solutions. Graduate thesis in Mechanical Engineering, National Cheng Kung University.
- [8] Hoyani S, Patel R, Oommen C, Rajeev R. (2017). Thermal stability of hydroxylammonium nitrate (HAN). Journal of Therm. Anal. and Calorim. 129: 2.
- [9] NIST Chemistry WebBook. <<https://webbook.nist.gov/chemistry>>