Temasek Defence Systems Institute

TDSI

Temasek Defence Systems Institute

Contact: tdsbox2@nus.edu.sg

Effect Of Humidity On Nitrocellulose At High And Low Temperatures

Cheow Wee CHIA, Dr Nathalie MAI, Dr Phil GILL

Introduction

A chemiluminescence technique has been used to measure the nitric oxide evolution from nitrocellulose (NC) samples at real-time. This technique offers clear advantages over conventional stability tests such as ageing and chemical analysis as it eliminates the need for high temperatures and long test time. It allows the measuring of decomposition rate at a temperature close to storage condition.

An inert carrier using nitrogen gas is constantly flushed over the NC sample to prevent any reaction between degradation products with the nitrocellulose sample. This setup is also known as a swept test (See Figure 1). The swept test is used to study the primary decomposition mechanism of NC (See Figure 2) under the influence of moisture over a range of temperature from 30 °C to 100 °C. Three different nitrogen (11.7 %,12.6 % and 13.55 %) content NC samples were studied.

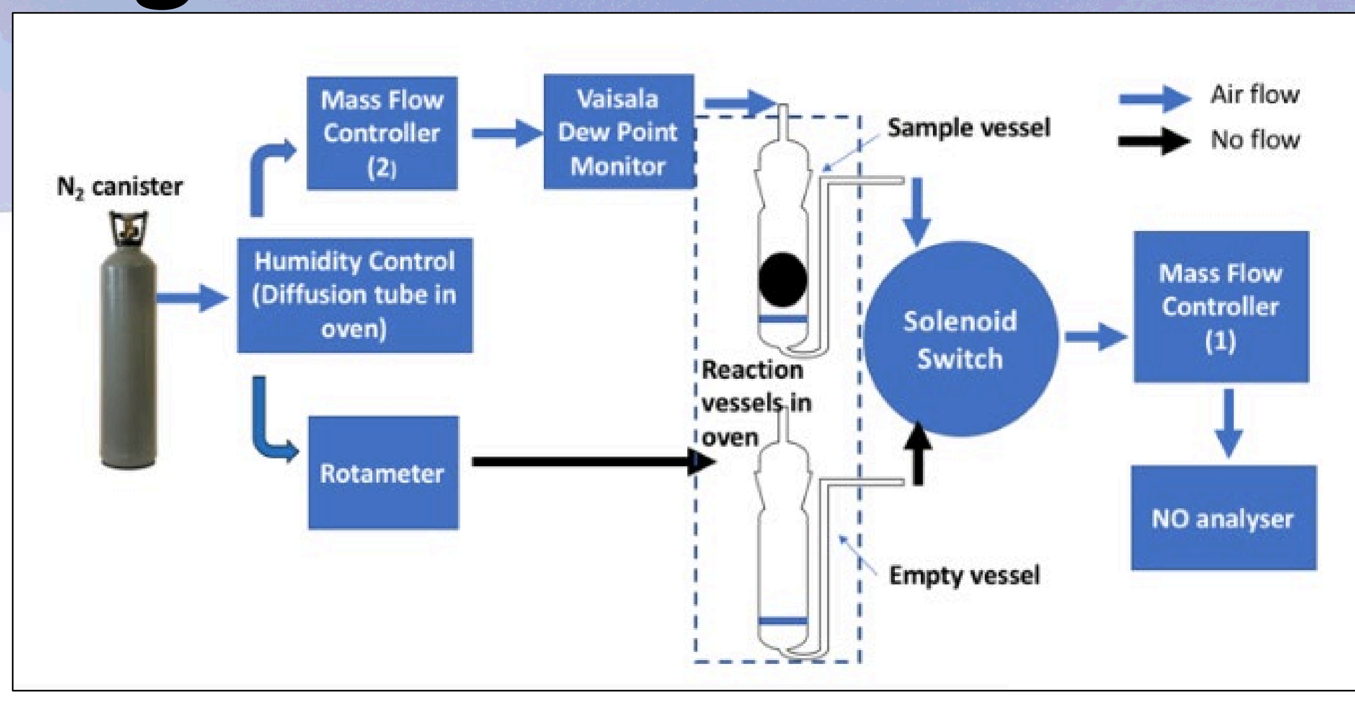

Figure 1: Experimental setup at "sample" mode where the carrier gas flows through the sample reaction vessel

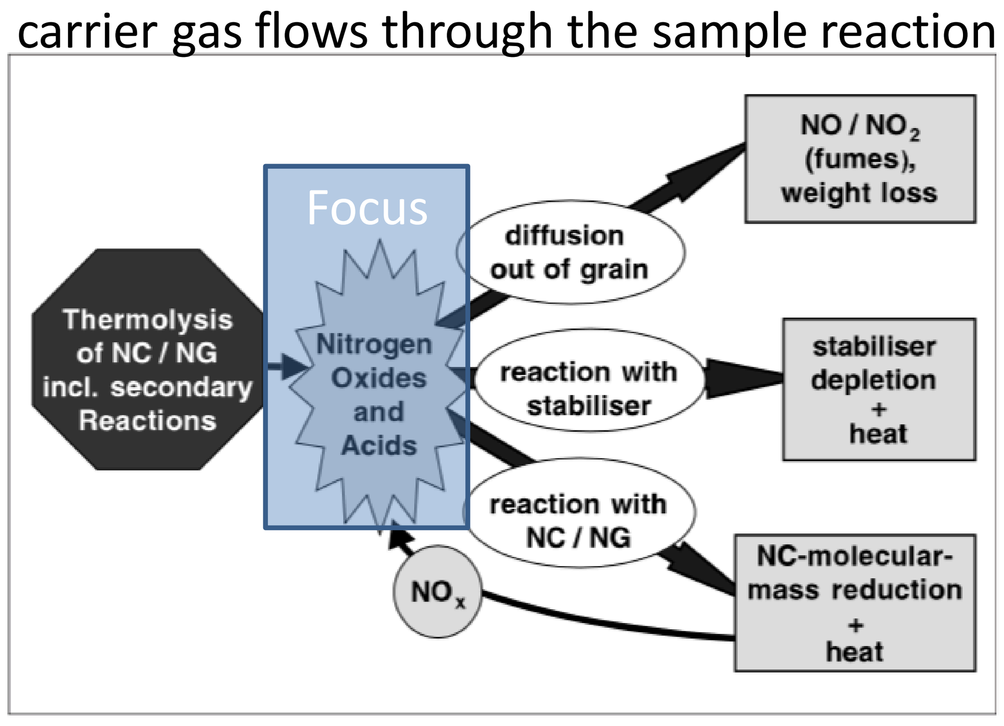

Figure 2: Research focus

Results and Discussions

Figure 3 shows that at low temperatures, as humidity increases from 700ppm to 1000ppm, the activation energy (E_a) decreases from 100kJ/mol to 59kJ/mol. The E_a recorded at 30°C-50°C were indicative of hydrolysis decomposition. A higher activation energy (Ea = 128kJ/mol), indicative of thermolysis was observed at 75°C -100°C. Changes in humidity does not impact the E_a of thermolysis.

Figure 4, Figure 5 and Figure 6 shows the plot on rate of decomposition vs humidity for NC with different nitrogen contents at low temperatures (30°C-50°C). In general, the results show the following trends: 1) the rate of NO evolution increases with increasing humidity, with a linear correlation, 2) the rate of NO evolution increases with increasing temperature, shown by the upward shift as temperature increases, and 3) the effect of humidity on the rate of NO evolution decreases, with increasing temperature, shown by the decreasing gradient of the graphs as temperature increases.

Figure 7 shows the E_a (extrapolated from Figures 4-6) of the three NC samples with different nitrogen content plotted against humidity. The graphs show that as humidity increases, the E_a decreases for all three samples. One interesting observation is that the E_a for both NC samples (12.6% and 13.55% nitrogen content) dropped to a very low value (~10kJ/mol), which cannot be explained adequately at this stage. Here, we expect to see more correlations between the nitrogen content in NC with E_a; however, no trends could be observed with the mixed results.

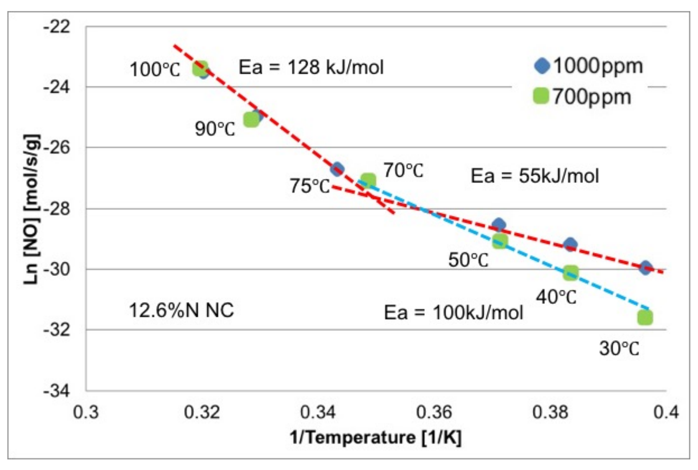

Figure 3: Arrhenius plot on NC with 12.6% nitrogen content at two different humidity levels

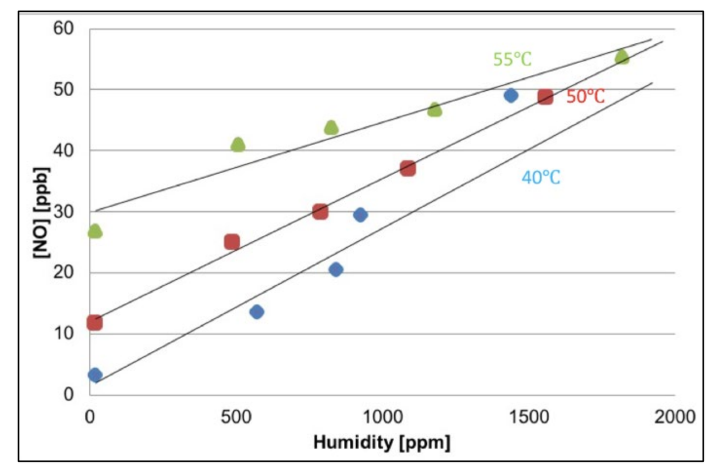

Figure 4: NC with 13.55% nitrogen content - rate of decomposition vs humidity

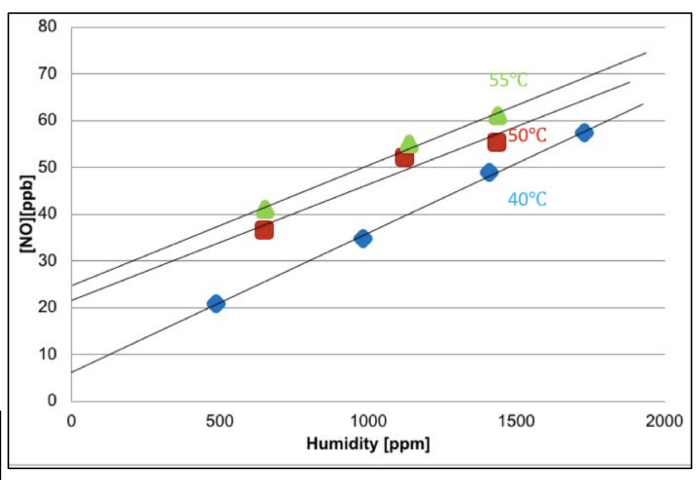

Figure 5: NC with 12.6% nitrogen content - rate of decomposition vs humidity

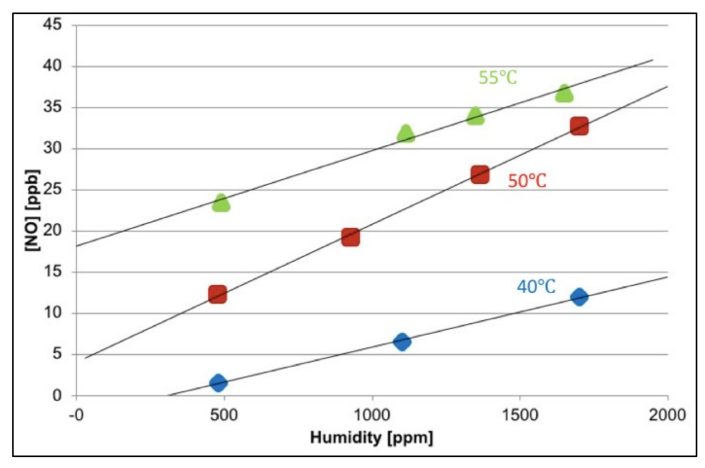

Figure 6: NC with 11.7% nitrogen content - rate of decomposition vs humidity

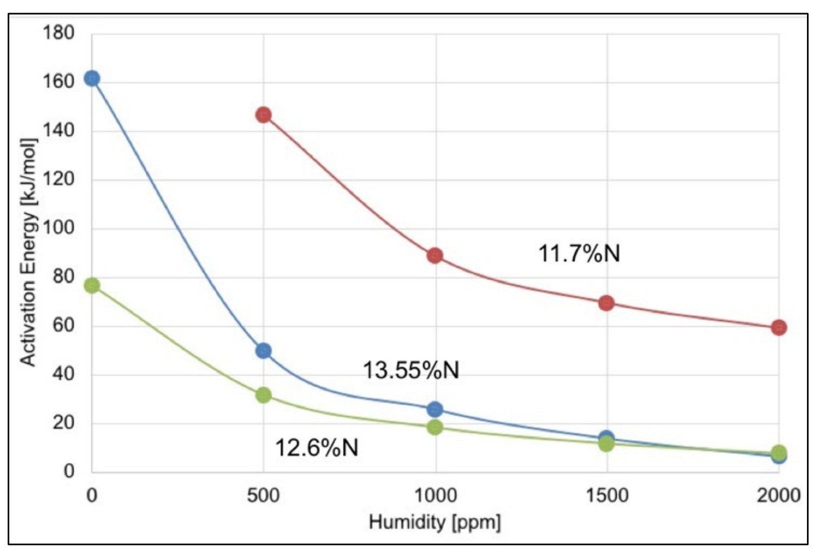

Figure 7: The effect of humidity on the activation energy of three NC with different nitrogen content at low temperatures

Conclusions

The present work established the impact of humidity at low temperatures (hydrolysis is dominant) is significant. This preliminary work suggests that humidity cannot be ignored as a control parameter when performing stability tests at low temperatures. Based on the chemiluminescent result of NO evolution, the following conclusions can be made:

- The amount of moisture had a little or insignificant impact on the rate of decomposition at higher temperatures, where the dominant decomposition mechanism is thermolysis.
- At lower temperatures, hydrolysis becomes the dominant decomposition pathway. Hence, the rate of decomposition increases with increasing moisture in a linear correlation.
- The effect of moisture on NC with different nitrogen content was not established due to mixed results. More tests are required to gather data points for reliable results.

This work uses only NO to estimate the degradation rate of NC and did not take measurement of the evolution of NO_2 . The existing setup can be easily configured by adding a NO_2 to NO converter to understand the full extent of NC degradation. In addition, this swept experiment only look solely at primary decomposition and discount the secondary decomposition reaction between the degradation products and the nitrate ester based explosive. However, it is possible to modify the current setup into a closed system and enable the investigation of secondary autocatalytic decomposition mechanisms. Here, we have proved that this method is highly sensitive and effective in measuring pure NC samples of various nitration levels, hence it would likely to be effective for NC based propellant and nitrate ester based formulation.

Acknowledgement

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