

## Study on mitigating ammonium nitrate fertiliser explosion hazards

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Ammonium nitrate (AN) is widely used in the fertiliser industry and is one of the most concentrated forms of nitrogen fertiliser. However, AN is associated with several types of hazards, including fire and explosion, which have occurred time and again in the past century; one example is the West fertiliser plant explosion that occurred on April 17, 2013, in West, Texas, USA. The explosion killed 15 people, injured at least 250 people, and damaged many buildings and homes. During the past century, there have been approximately 40 accidents associated with AN throughout the world. Despite specific regulations and rules on AN from various agencies, the accidents continue to occur. Extensive research has been conducted on this area; however, limited understanding exists of the underlying causes of detonation of AN. AN explosivity can be reduced by various conditions, such as the existence of specific additives (some materials change the chemical reaction pathways, inhibiting explosion) or the effect of thermal pre-treatment history. The main objective of this research is twofold: first, to look into the behavior of AN with sodium sulphate as an additive; and second, to examine the effect of its thermal history to determine how the storage temperature and its variations will affect decomposition of AN. The Reactive Systems Screening Tool (RSST) has been employed to study the runaway behavior of AN with sodium sulphate or pre-treated AN sample. The sample weight that the RSST can handle is approximately 3 g – 10 g, larger by approximately 3 orders of magnitude than the capacity of the Differential Scanning Calorimeter (DSC) which can measure a few milligrams of sample. Important parameters from the experimental results are reported such as “onset” temperature and self-heating rate. The results showed that both the presence of sodium sulphate and the thermal pretreatment of AN exert an inhibiting effect on AN thermal decomposition. The findings of this work agree with the work performed in literature which is essentially based on DSC experiments.

Keywords: ammonium nitrate, runaway reaction, West explosion, RSST, sodium sulphate, and explosion mitigation

### Introduction

Ammonium nitrate (AN) and other compounds of its family are widely used in the fertiliser industry (Zygmunt and Buczkowski, 2007) as one of the most concentrated forms of nitrogen fertiliser (35% N). It is popular because it is very soluble in water, and hence in the soil, and the nitrate can move deep into the root zone of vegetation under wet conditions. Furthermore, AN fertiliser and AN-based fertilisers are relatively inexpensive. AN can also be used as explosive or agent for making explosives such as ammonium

nitrate / fuel oil (ANFO) (Marlair and Kordek, 2005). Usually, under atmospheric conditions, AN is considered as a nonflammable chemical or a noncombustible material (Marlair and Kordek, 2005; Texas, 1947). However, under the right conditions, it behaves as a strong oxidizing agent, resulting in detonation, threatening people's lives and causes property losses (EPA, 1997; HSE, 1996).

Fires and explosions associated with AN have been occurring throughout history. The most recent incident happened at the West fertiliser plant, in Texas, USA, on April 17, 2013, killing 15 people and injuring at least 250 people (CBSNews, 2013). The resulting blast-wave completely destroyed the entire facility and caused various levels of damage to many buildings, businesses, and homes at significantly long distances from the plant. There were more than 50 homes, a 50-unit apartment building, a nursing home, and four schools located in the impact zone, which was within around 600 m of the plant. Similarly, on September 21, 1921, in Oppau, Germany, an AN explosion involving 450 tons of AN-based fertiliser caused 561 fatalities, 1952 injuries, and left 7500 people homeless (French Ministry of Environment, 2008). The fertiliser used in Oppau was a mixture of AN and ammonium sulphate with a ratio of 50:50. The root cause of the accident was that people tried to disaggregate caked fertiliser mixture by using industrial explosives. The method of disaggregation had been used over 20,000 times without any incident. The explosion created a (90 m) X (125 m) crater with a 20 m depth. According to the witnesses, there were two successive explosions, the first one being weak and the second one devastating. According to what was reported in the New York Times (dated 29 January 1922), the material loss was approximately 321,000,000 marks, *i.e.*, 1.7 million US dollars, 1.24 million euros, or 1.04 million GBP.

Another explosion occurred on September 21, 2001, in the AZF (Azote de France) fertiliser factory in Toulouse, France (Dechy *et al.*, 2004), involving 300 tons of AN, resulting in 30 deaths and 2242 injuries. At the time the accident occurred, there was no pump or no heat source. AN contaminated with sodium dichloroisocyanurate (*i.e.*, DCCNa) was determined to be the root cause of this incident (Li and Koseki, 2005). The off-specification granular AN was stored flat in a warehouse between process parts, and was separated by partitions when the explosion occurred. The explosion created a crater of 10 meters in depth and 50 meters in width. The resulting blast wave affected windows up to 3 kilometers away from the factory. The material damage was believed to be 2.3 billion euros, *i.e.*, 3.17 billion US dollars or 1.93 billion GBP (Barthelemy *et al.*, 2001).

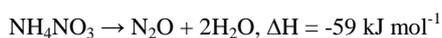
In the US, the Occupational Safety and Health Administration (OSHA) has specific regulations that apply to the use of AN, such as the Explosives and Blasting Agents Standard (29 CFR 1910.109). Furthermore, general requirements of OSHA include the "General Duty Clause" of the Occupational Safety and Health Act (P.L. 91-596, as amended), the Hazard Communication Standard (29 CFR 1910.1200), and an Emergency Action Plan (EAP) according to OSHA Standard 1910.38. The Environmental Protection Agency (EPA) also has a general duty clause and specific regulations that apply to facilities that handle AN, including the Emergency Planning and Community Right to Know Act (EPCRA) and Section 112(r) of the Clean Air Act (CAA). The Department of Homeland Security (DHS) regulations include the proposed rule regulating the control of the purchase and the sales of AN (Section 563) and the Chemical Facility Anti-Terrorism Standards (CFATS). The Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF) regulates AN based blasting agents with regulations on the necessary distance to be maintained between AN and other explosive materials.

In the UK, two of the most relevant regulations that control the manufacture, importation, storage, and transportation of AN fertiliser

include the Ammonium Nitrate Materials (High Nitrogen Content) Safety Regulations 2003 (AN Safety Regulations) and the Control of Major Accident Hazards Regulations 1999, as amended (COMAH).

In literature, AN has been studied by various types of calorimeters. However, because different types of equipment have different levels of accuracy, the detected “onset” temperatures of decomposition depend strongly on the performance of the calorimeter. Different “onsets” may be reported when using different equipment, meaning there is not a consistent “onset” temperature available. The reaction is always occurring at the molecular level, but the rate of the reaction can only be measured after a certain temperature value, *i.e.* the “onset” temperature. Depending on the sensitivity of the equipment to trace a predetermined heating rate (or temperature rise rate), different “onset” temperatures of AN have been reported in literature, for instance 210 °C (HSE, 1996), 200 °C (MacNeil *et al.*, 1997; Oxley, Kaushik, and Gilson, 1992), and 190 °C (Turcotte *et al.*, 2003).

Different reaction pathways of AN have been reported, out of which the most accepted reactions are listed below (Brower, Oxley, and Tewari, 1989; Feick and Hainer, 1954; Saunders, 1922).



The existence of other chemicals can affect the thermal behavior of AN. Some chemicals, called inhibitors, mitigate AN explosion by either behaving as inert materials or by changing the reaction conditions (Oxley *et al.*, 2002). To ensure the agricultural benefit, such chemicals should not harm vegetation. The present work reports the findings of the effect of selected conditions on AN explosivity. Sodium sulphate can be used as a fertiliser. Janzen and Bettany (1986) have applied sodium sulphate on crops to test the release rate of sulfur. Therefore sodium sulphate has been chosen to be mixed with AN in order to study its impact on AN thermal decomposition. In addition the effect of thermal history of AN, which may influence its behavior, has been studied. In storage areas, the temperatures may vary at different time periods in one day, thus affecting the material behavior. The thermal decomposition of an AN mixture with sodium sulphate, as well as thermally pre-treated pure AN have been studied using a Reactive System Screening Tool (RSST). The results obtained are compared with the decomposition of thermally untreated pure AN.

## Experiments

### Chemicals

Ammonium nitrate (VWR Reagent, ACS Grade, 99.9% assay) and Sodium sulphate (Aldrich, 99+%, ACS Reagent) were used without further purification.

### Reactive Systems Screening Tool (RSST)

The RSST is a pseudo-adiabatic calorimeter manufactured by Fauske and Associates. It can measure temperatures up to 500 °C and pressures up to 490 psi, with a relatively low thermal inertia factor which can be as low as 1.04 (Fauske, 1994). In the RSST, the test cell (with a volume of 10 ml) is surrounded by a double bottom heater fixed in the insulation sheath and placed in the containment

vessel (with a volume of approximately 350 ml). The test cell is open and the containment vessel is closed. A thermocouple is placed inside the test cell and connected to the control system. A pressure transducer is placed outside the containment vessel. Usually the RSST is pressurized with an inert gas to reduce evaporation of samples whenever applicable. Figure 1 shows the schematic diagram of the RSST. The heating rate can be programmed as desired. In the present study it was varied from  $0.25\text{ }^{\circ}\text{C min}^{-1}$  to  $2\text{ }^{\circ}\text{C min}^{-1}$ . During operation, the temperature and pressure of the sample are recorded and logged with the computer. The self-heating rate of exothermic reactions, which is also the rate of temperature rise, and the pressure rise rate are calculated and presented as a function of the sample temperature (Fauske, 1998). More information about how the RSST functions can be found in literature (Fauske, 1998; Grolmes, Leung, and Fauske, 1989).

The RSST has been used by our research team to study other reactive chemical systems such as hydroxylamine (Wei, Rogers, and Mannan, 2006; Wei *et al.*, 2004) and di-tert-butyl peroxide (DTBP) in toluene (Aldeeb, Rogers, and Mannan, 2002). Moreover, to the best of our knowledge, our research team is the first to study AN using this equipment.

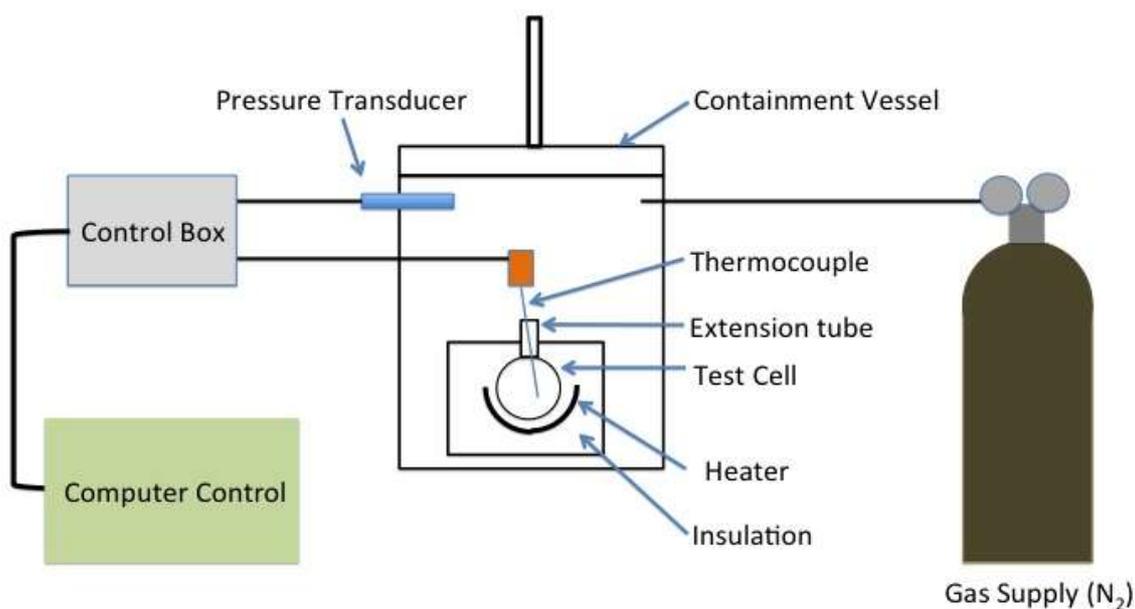


Figure 1: The schematic diagram of the RSST (Han *et al.*, 2013).

In the experiments performed in this research, approximately 3 g – 5 g of solid samples were prepared and tested using the RSST. Each experiment was repeated two or three times.

An initial backpressure of 187 psig was applied to the test system using a gas composed of 98.47% nitrogen and 1.53% oxygen. Generally, there are three main reasons behind the application of the backpressure. First, whenever applicable, the initial pressure is applied to prevent liquid boiling of the sample, to reduce material loss. Second, it can simulate high-pressure conditions, helping data analysis of AN decomposition in a confined space. Third, in the case of an AN pile that is high in height, there is usually pressure build-up at the bottom of the pile. By assuming AN particles behave as fluids, a rough estimation reveals that a 1 meter increase in

the pile results in an increase of 2.3 psi in the pressure at the bottom of the pile.

In this work, different heating rates were applied during different temperature ranges. For temperatures from ambient temperature up to 150 °C, the heating rate was 2 °C min<sup>-1</sup>; for temperatures from 150 °C to 180 °C, the rate was 1 °C min<sup>-1</sup>; and for temperatures from 180 °C up to 340 °C, the rate was 0.5 °C min<sup>-1</sup>. In all the experiments, the shutdown limit for temperature was 410 °C, and the pressure shutdown limit was 400 psig.

The results of each experiment are reported in the form of important parameters such as “onset” temperature, maximum self-heating rate, and temperature at maximum self-heating rate. The figures were drawn based on the experimental results, including temperature versus time, pressure versus temperature, and logarithmic plot of self-heating rate versus temperature profiles. The activation energy and heat of reaction of pure AN were also measured experimentally and are reported here.

## Experimental procedure

To study pure AN thermal decomposition behavior, 3.5 g of pure AN was weighed and tested in the RSST using the back pressure and heating rate described in section 2.2.

The next step was study the behavior of an AN mixture with sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>). The experimental procedure consists on loading the test cell with 3.5 g of solid AN and various amounts of Na<sub>2</sub>SO<sub>4</sub>, more precisely with 0.1 g, 0.3 g, and 1.0 g. Once the mixture was loaded into the test cell, the cell was vigorously shaken in all directions for at least 8 minutes until the sample was well mixed.

To study the effect of thermal history, the pure AN sample was pre-treated by heating up the sample. First, 3.5 g of pure solid AN was weighed and loaded in the test cell and then pre-heated in the RSST. In order to pre-treat the sample, a different heating rate program than the one reported above was employed. For temperatures from ambient temperature up to 50 °C, the heating rate was 2 °C min<sup>-1</sup>; for temperatures from 50 °C to 80 °C, the rate was 1 °C min<sup>-1</sup>; and for temperatures from 80 °C up to 100 °C, the rate was 0.25 °C min<sup>-1</sup>. It took approximately 125 minutes in total to heat up the sample to 100 °C. When 100 °C was reached, the sample was cooled down by ambient temperature to room temperature. This completed the pre-treatment process. The RSST was vented and the sample was then heated in order to decompose following the procedure described in section 2.2.

## Results and discussion

### Pure AN experiment

In our previous work (Han *et al.*, 2013), pure AN was studied using the RSST, and the results were reported. The temperature profile, self-heating rate, pressure profile, and pressure rise rate profile of three replicate pure AN experiments were shown and discussed. The thermal decomposition of pure AN can be detected by the RSST at approximately 200 °C, when both the temperature and pressure start to increase very rapidly. In this work, the “onset” temperature is defined based on the logarithmic plot of the self-heating rate. Figure 2 is a logarithmic plot of the self-heating rate of pure AN decomposition. As can be seen in Figure 2, when the

self-heating rate starts to increase, a tangent is drawn. In the meantime, a straight line is drawn on the end of the self-heating rate curve before it starts to increase rapidly. The intersection of the two lines is the point which is the reported “onset”. The maximum self-heating rate,  $(dT/dt)_{\max}$ , is the maximum rate of temperature rise recorded during the whole experiment process.

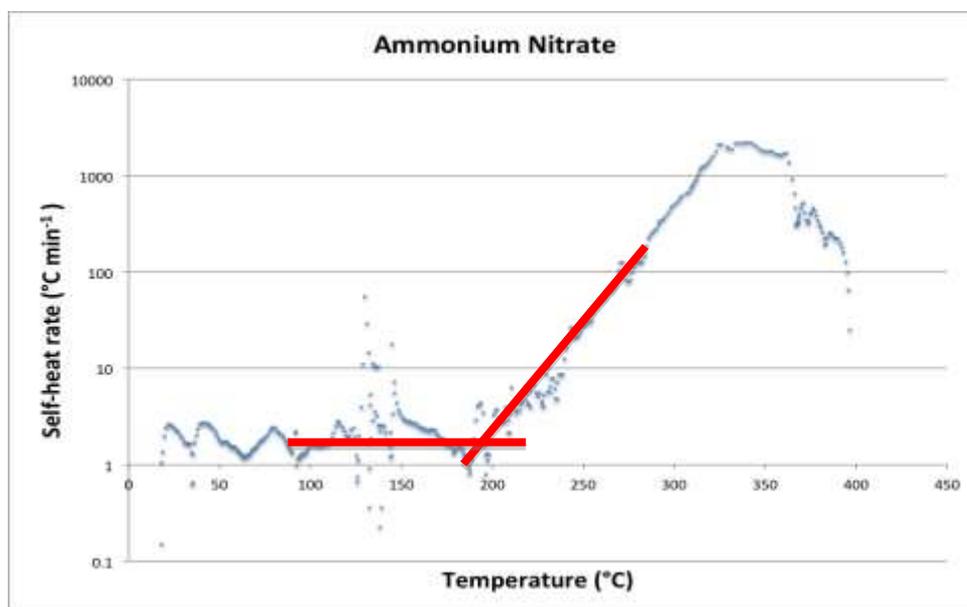


Figure 2: Determining the “onset” temperature.

Using the RSST, the “onset” temperatures for the three replicate experiments were identical, while the time to detect “onset” was usually different. The rationale behind this could be that there is only one thermocouple in the RSST which is located at the center of the bottom of the test cell. During the experiments, the heating rate and heat distribution within the sample might not be homogeneous. Despite the difference, the overall trends and critical parameters were almost the same for replicate experiments.

For pure AN, the “onset” temperature is  $200 (\pm 10)$  °C. The maximum self-heating rate is  $82 (\pm 17)$  °C s<sup>-1</sup>, which occurred at the temperature of  $347 (\pm 17)$  °C.

In this study, the thermal inertia factor,  $\phi$ , was calculated using Equation (1) and was found equal to 1.2.

$$\phi = 1 + \frac{m_c \cdot C_{p,c}}{m_s \cdot C_{p,s}} \quad (1)$$

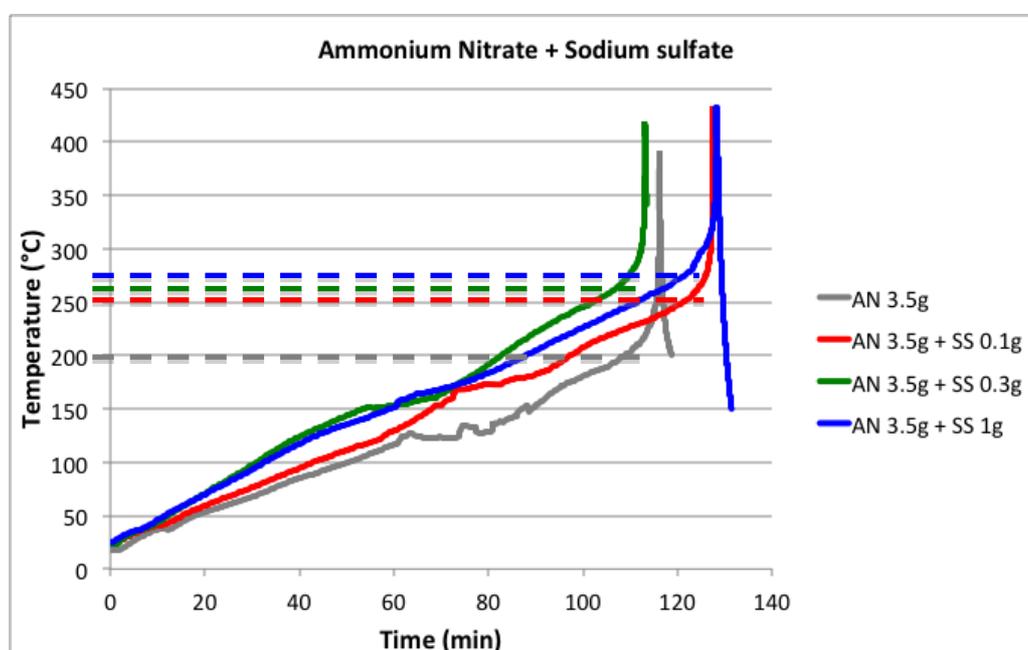
where  $m$  is the mass,  $c_p$  is the heat capacity, and subscript  $s$  and  $c$  respectively stand for the sample and the cell.

Based on the theory of Townsend and Tou (1980), after a simplified calculation, the average activation energy of pure AN decomposition is approximately  $66 (\pm 5)$  kJ/mol, and the heat of reaction is  $-32 (\pm 5)$  kJ/mol.

### Effect of additive - AN and sodium sulphate experiment

To study the effects of additives, AN was mixed with sodium sulphate. If the “onset” temperature of the mixture is higher than the “onset” temperature of pure AN, the additive is defined as an inhibitor. This is because when the additive is mixed with AN, the “onset” behavior of AN is delayed. In the present study, the “onset” temperature of pure AN was found to be 200 °C.

As mentioned earlier, in this study, pure solid AN was mixed with three different concentrations of  $\text{Na}_2\text{SO}_4$ . The concentrations of  $\text{Na}_2\text{SO}_4$  tested included 2.8 wt.%, 7.9 wt.%, and 22.2 wt.%. The melting point of AN is 169 °C (Kestilä, Harju, and Valkonen, 1993). The melting point of  $\text{Na}_2\text{SO}_4$  is 884 °C, much higher than the temperature range used in this work, therefore, there was always a residue remaining after each experiment. The temperature vs. time profiles and the pressure vs. temperature profiles of the three experiments are shown in Figure 3(a) and Figure 3(b), respectively. The self-heating rate profile, which is also the rate of temperature rise profile, is shown in Figure 4(a). Since this work determines the “onset” temperature from the self-heating rate profile, it is important to have a better view of the self-heating rate profile. Part of Figure 4(a) is enlarged and shown in Figure 4(b), where the data between 240 °C to 300 °C of the tests are shown. Accessorial lines are also added in Figure 3(a) and Figure 4(b) to indicate the respective “onset” temperatures for each curve. In all these figures, the experimental data of the pure AN thermal decomposition are also given as a reference, to enable easier comparisons.



(a)

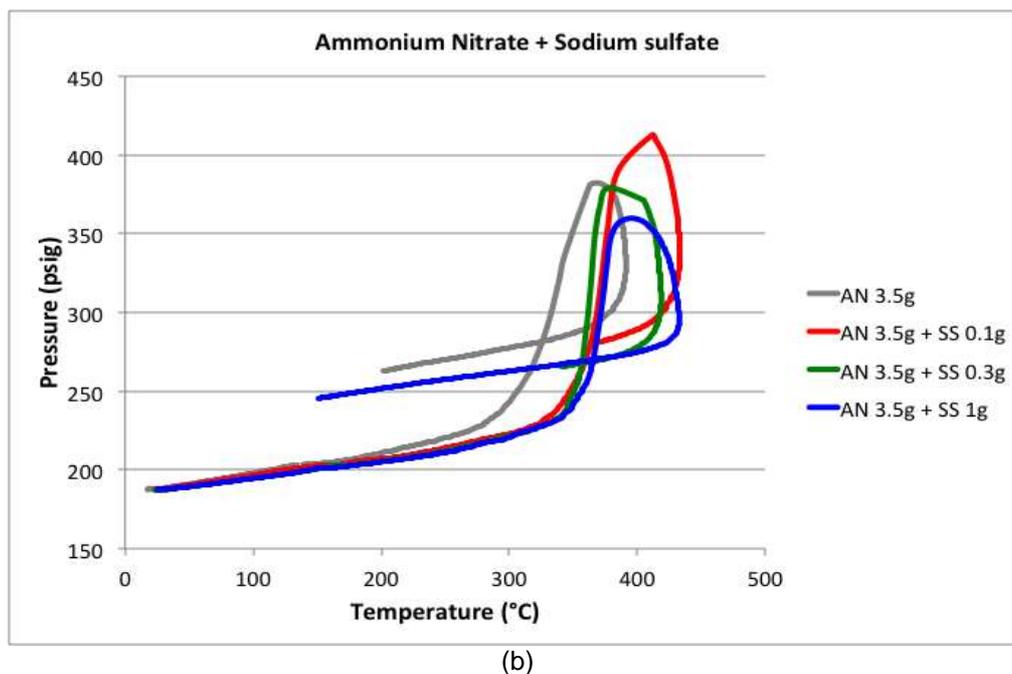


Figure 3: The thermal decomposition of AN, using  $\text{Na}_2\text{SO}_4$  as an additive. (a) Temperature profile (b) Pressure – temperature profile.

As can be seen in Figure 3(a), the temperature vs. time profile, the temperature curves of the three mixtures increase relatively smoothly compared with pure AN temperature profile (grey line), which shows significant temperature fluctuations between 125 °C and 150 °C. The reason is that at 125 °C, pure AN changes from phase II to phase I; via an endothermic process. In the pure AN experiments, the temperature decreases by 5 °C after reaching 125 °C, and then it starts to increase again to the point where the exothermic reaction accelerates rapidly. However, when  $\text{Na}_2\text{SO}_4$  is mixed with AN, this endotherm does not become measurable by the RSST. The “onset” temperatures of all the three experiments performed with  $\text{Na}_2\text{SO}_4$  were higher than 200 °C, which is the “onset” temperature of pure AN thermal decomposition. Therefore, it can be concluded that  $\text{Na}_2\text{SO}_4$  is an inhibitor for AN. The curves of the three temperature profiles look similar, indicating that decomposition reaction pathways of the mixtures of AN with  $\text{Na}_2\text{SO}_4$  in various concentrations may be the same. The variation of the time to detect “onset” varies because of the inherent problem of the RSST described earlier in section 3.1.

As can be seen in Figure 3(b), before the temperature reaches 200 °C, all four experiments (including the pure AN experiment) have almost the same pressure at the same temperature. However, after 200 °C and above 200 psig, at each temperature, the pressures of all three mixtures of AN with  $\text{Na}_2\text{SO}_4$  are still almost identical until the “onsets” are detected, but different from the pressure of pure AN. This is most likely caused because of different reaction pathways being followed by AN with and without  $\text{Na}_2\text{SO}_4$ , as indicated by the fact that the end pressure is also different. When the reactions finish, the pressures start to decrease. At this stage, the pressure data of the three mixtures differ when the temperatures are above 350 °C and pressures are above 270 psig. This is most likely because the transducer cannot record fast enough the rapidly dropping pressure. It is also found that in general, the more  $\text{Na}_2\text{SO}_4$  there is in the mixture, the lower the maximum pressure reached and with small differences, the lower the end pressure of the sample after cooling to ambient temperature.

As can be seen in Figure 4(a) which shows the self-heating rate profile, the more  $\text{Na}_2\text{SO}_4$  is present in the mixture, the higher the

“onset” temperature is recorded. For all the experiments, the “onset” temperatures, maximum self-heating rates ( $(dT/dt)_{max}$ ), and the temperatures at the maximum self-heating rate are summarized here. It is concluded that with only a small addition of  $\text{Na}_2\text{SO}_4$ , the “onset” temperature can be greatly increased. For example, when 2.8 wt.% of  $\text{Na}_2\text{SO}_4$  is mixed with AN, the “onset” temperature is 251 °C (51 °C higher than pure AN), and the maximum self-heating rate is 116 °C s<sup>-1</sup>, which occurred at the temperature of 377 °C; when 7.9 wt.% of  $\text{Na}_2\text{SO}_4$  is mixed with AN, the “onset” temperature is increased by 60 °C, and the maximum self-heating rate is 110 °C s<sup>-1</sup>, which occurred at the temperature of 377 °C; and when 22.2 wt.% of  $\text{Na}_2\text{SO}_4$  is mixed with AN, the “onset” temperature is increased by 75 °C, and the maximum self-heating rate is 68 °C s<sup>-1</sup>, which occurred at the temperature of 394 °C.

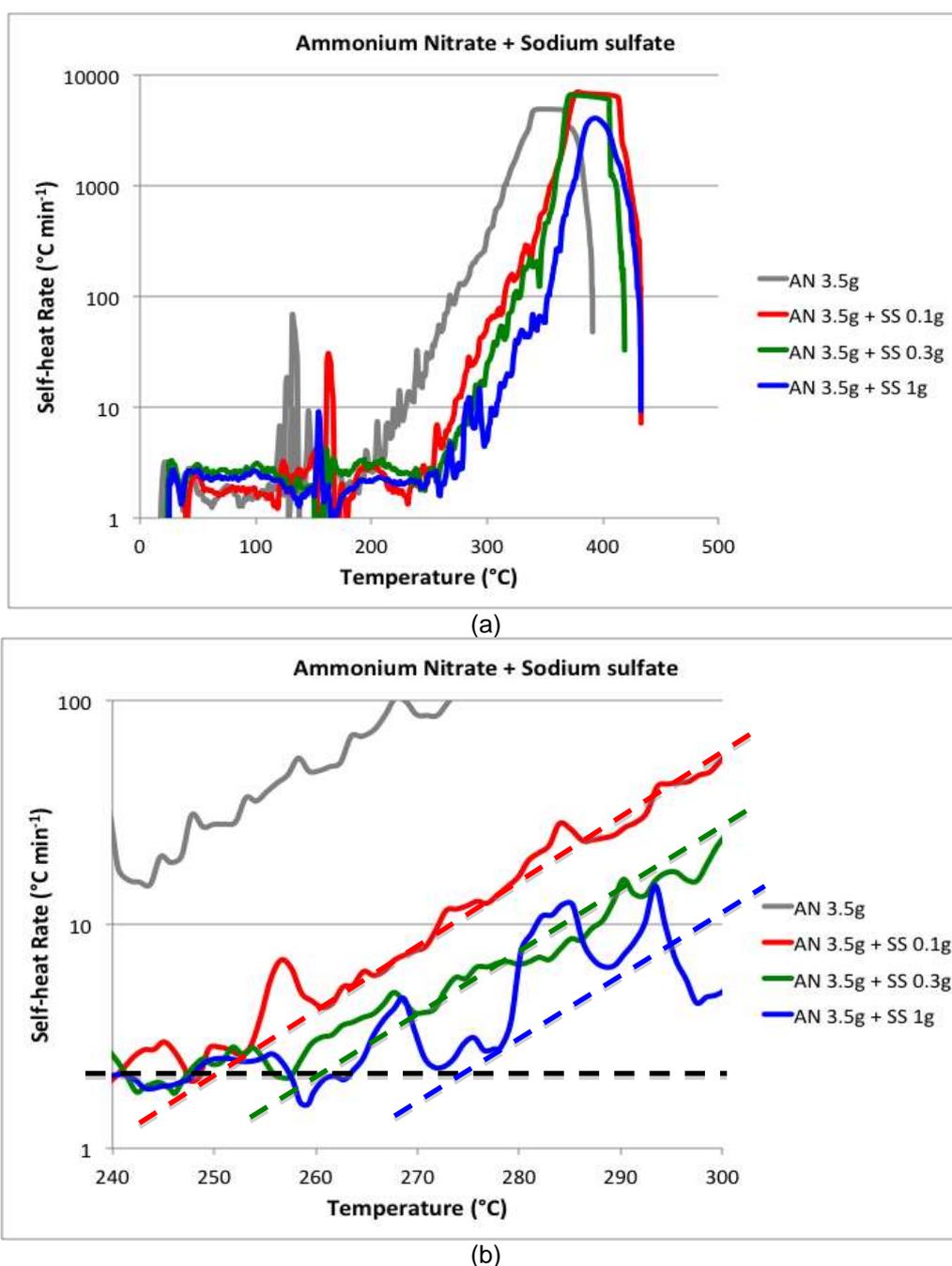


Figure 4: The thermal decomposition of AN, using  $\text{Na}_2\text{SO}_4$  as an additive. (a) Self-heating rate (b) Enlarged self-heating rate profile.

According to aforementioned data, it can be concluded that in general, the addition of  $\text{Na}_2\text{SO}_4$  will result in a higher maximum self-heating rate than pure AN when less than 22.2 wt.% of  $\text{Na}_2\text{SO}_4$  is used. When 22.2 wt.% is used, the maximum self-heating rate is lower than pure AN. More concentrations will be tested to find out the threshold at which the amount of  $\text{Na}_2\text{SO}_4$  can result in the same maximum self-heating rate as pure AN and the increase of the “onset” temperature as a function of added mass. In most cases, the mixture with a higher concentration of  $\text{Na}_2\text{SO}_4$  has a lower value of maximum self-heating rate than the mixture with a lower concentration of  $\text{Na}_2\text{SO}_4$ . Based on Figure 4(a), the maximum self-heating rates of the three mixtures occur at almost the same temperature range, around 380 °C to 390 °C, which is higher than the temperature of pure AN (approximately 350 °C). The temperature at the maximum self-heating rate of AN decomposition is increased by approximately 40 °C with the addition of  $\text{Na}_2\text{SO}_4$ . However, the reactions occur very fast and the temperatures change fast accordingly. Therefore, the RSST may only record a few points in this period. The recorded temperatures may not be the actual temperatures at the maximum rates. In Figure 4, the curves are drawn based on the few data points.

By comparing the results obtained for the mixtures of AN with  $\text{Na}_2\text{SO}_4$  against pure AN, it is clear that the “onset” temperatures are increased and the temperatures at maximum self-heating rate are increased. This shows that the existence of  $\text{Na}_2\text{SO}_4$  as an additive delays the runaway behavior of pure AN. The more  $\text{Na}_2\text{SO}_4$  mixed with AN, the higher the “onset” temperatures detected. As a conclusion, sodium sulphate is a good inhibitor for AN.

In our previous work (Han *et al.*, 2013), analysis of an AN mixture with 2.78 wt.% of  $\text{Na}_2\text{SO}_4$  is given with more details. Oxley *et al.* (2002) also point out that  $\text{Na}_2\text{SO}_4$  behaves as an inhibitor by using the DSC. Based on their results, when AN is mixed with 5 wt.%  $\text{Na}_2\text{SO}_4$ , the decomposition exotherm is raised by 7 °C; when AN is mixed with 20 wt.%  $\text{Na}_2\text{SO}_4$ , the decomposition exotherm is raised by 23 °C.

### **Effect of thermal history – AN pre-treatment**

In order to study the effect of thermal history, to be specific, how temperatures affect the characteristics of AN, an AN sample was pre-heated as described in section 2.3. In this section, the thermal decomposition of pre-treated pure AN is described. The temperature vs. time profile and self-heating rate profile of two replicate pre-treatment experiments are shown in Figure 5(a) and (b), respectively. The experimental data of pure AN test is also given as a reference in both the figures.

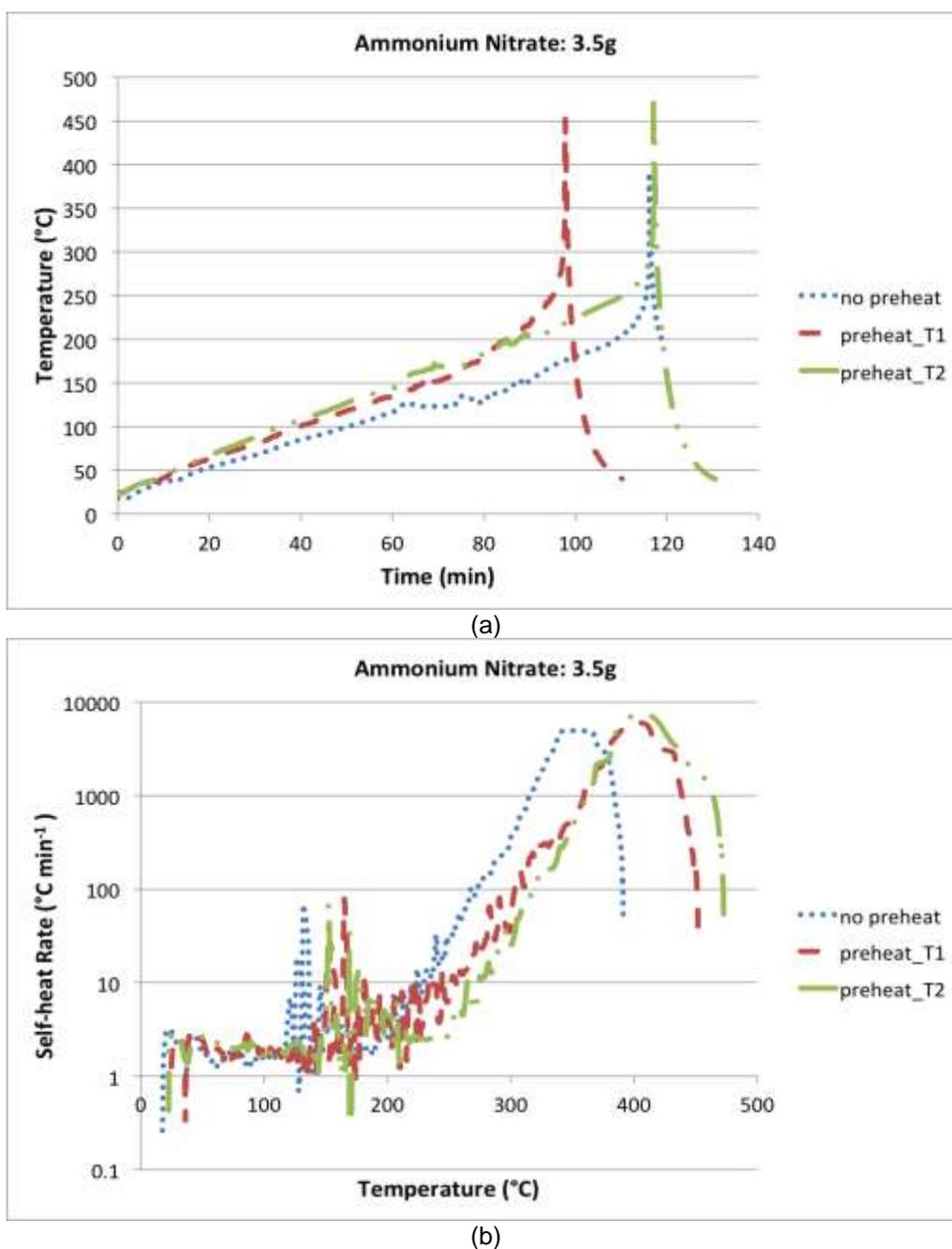


Figure 5: The thermal decomposition of pre-treated AN. (a) Temperature profile (b) Self-heating rate.

As can be seen from Figure 5(a), the temperature profiles of the two replicate experiments for AN with pre-treatment are identical before the temperatures reach 200 °C. After that, the time to reach “onset” is different for the two replicate experiments. That is most likely caused by the inherent problem of the RSST in testing solid samples as described before, in section 3.1. The “onset” temperatures obtained in the two experiments are relatively close. The overall trends and critical parameters are also almost the same. Unlike pure AN, the temperature and the pressure of the pre-treated AN do not start to increase dramatically immediately after 200 °C. This can be seen more clearly from the logarithmic plot of the self-heating rate profile in Figure 5(b). More research is currently underway to determine the reason why an increase in the “onset” temperature would occur in the pre-heated AN.

From the results, the pre-treatment of heating AN will mitigate the hazards of AN decomposition by inducing the reactions to occur at higher temperatures than AN without the treatment. The “onset” temperature of the pre-treated AN is 247 (±6) °C, with the

maximum self-heating rate of  $113 (\pm 18) \text{ }^\circ\text{C s}^{-1}$ , which occurs at  $404 (\pm 6) \text{ }^\circ\text{C}$ .

By comparing the results obtained for pre-treated AN against AN without pre-treatment, it is found that the “onset” temperature is increased by  $47 \text{ }^\circ\text{C}$ , and the temperature at maximum self-heating rate is increased by  $57 \text{ }^\circ\text{C}$ . The results indicate that the pre-treatment helps to mitigate the runaway behavior of AN. This could also be caused by the removal of water from the samples. It took approximately 12 hours between each thermal pre-treatment and decomposition, therefore the samples with thermal pre-treatment contain much less water than AN without the pre-treatment process. The reasons behind this need further research.

## Conclusions

In this work, the RSST has been used to study the runaway behavior of solid AN mixture with sodium sulphate and thermally pre-treated pure AN. It can be concluded that by adding sodium sulphate to AN, the “onset” of AN decomposition will be increased. When sodium sulphate is mixed with AN, both the “onset” temperatures and temperatures at maximum self-heating rate will increase. The more sodium sulphate in the mixture, the more obvious the inhibiting effects are. To be specific, greater concentrations of sodium sulphate result in higher “onset” temperatures. For example, the “onset” temperature is  $251 \text{ }^\circ\text{C}$  when AN is mixed with 2.8 wt.% of sodium sulphate, which is  $51 \text{ }^\circ\text{C}$  higher than the “onset” temperature of pure AN; the “onset” temperature is  $275 \text{ }^\circ\text{C}$  when AN is mixed with 22.2 wt.% of sodium sulphate, which is  $75 \text{ }^\circ\text{C}$  higher than the “onset” temperature of pure AN. As a conclusion, sodium sulphate is a good inhibitor for AN. The addition of sodium sulphate may affect the reaction pathway of AN, which needs further study. The pre-heated AN also increased the “onset” temperatures and temperatures at maximum self-heating rate of AN. Using the pre-treatment method presented in this work, the “onset” temperature of AN thermal decomposition was increased by approximately  $50 \text{ }^\circ\text{C}$  compared with that of pure AN. The RSST used in this study is a preliminary screening tool. Compared with other calorimeters such as the Automatic Pressure Tracking Adiabatic Calorimeter, it has less accuracy. Therefore, more work needs to be done to obtain more quantitative results. More detailed results and the investigation of science behind the behavior of the above and alternative inhibitors or the methods of pre-treatment will provide a great benefit to the AN fertiliser storage.

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