Ammonium Nitrate Thermal Decomposition with Additives

Zhe Han¹, Sonny Sachdeva¹, Maria I. Papadaki², M. Sam Mannan*¹

¹ Mary Kay O’Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, USA
² Department of Environmental and Natural Resources Management, School of Engineering, University of Patras, Seferi 2, Agrinio 30100, GREECE

Abstract
Runaway reactions present a potentially serious threat to the chemical process industry and the community as these incidents occur time and again. The main objective of this research is to study the root causes associated with ammonium nitrate (AN) explosions during storage, specifically the effects of additives, while maintaining its agricultural benefit. Reactive Systems Screening Tool (RSST) has been used for reactivity evaluation and to better understand the mechanisms that result in explosion hazards. The results obtained from this tool have been reported in terms of onset temperature, rate of temperature and pressure rise, and the maximum temperature. The runaway behavior of AN in solid form and water solution has been tested, as well as an AN mixture with additives to study the effect of contamination. Multiple tests have been conducted to determine the characteristics of AN decomposition. The results show that the presence of sodium sulfate (Na₂SO₄) can increase the onset temperature of AN decomposition; while potassium chloride (KCl) tends to decrease the onset temperature.

Keywords:
Ammonium nitrate (AN); Decomposition; Inhibitor; Promoter; Water; Reactive Systems Screening Tool (RSST).

1. Introduction
Ammonium nitrate (AN) is widely used both as a fertilizer and an explosive material [1]. As a fertilizer, it is an excellent source of nitrogen. As an explosive, AN is mixed with fuel oil, called ammonium nitrate fuel-oil (ANFO) [2]. AN is not considered a flammable chemical or combustible material at atmospheric temperatures [2, 3]. However, it is a strong oxidizing agent that can detonate under certain conditions which include elevated temperature, presence of impurities, and confinement [4, 5]. The hazard types [2] of AN are fire related (as an oxidizer), self-sustained decomposition (SSD) [6], and explosion hazards. Explosions associated with AN have occurred throughout history, the most recent of which happened on April 17, 2013, in West, Texas, USA. In this explosion, 270 tons [7] of AN was involved, which killed 15 people and
injured more than 250 people [8]. On September 21, 1921, in Oppau, Germany, an AN explosion caused 561 fatalities, which involved 450 tons of AN [9]. Contamination was believed to be the root cause of that accident [9]. Another shocking AN explosion happened on April 16, 1947, in Texas City, Texas, USA, which resulted in 581 fatalities. There were 2300 tons of AN in this explosion, which was caused by fire [3]. The Toulouse disaster occurred on September 21, 2001, in France [10], involving 300 tons of AN resulting in 30 deaths. AN contamination with chloride was determined to be the root cause of this incident. The Oklahoma City [11] terrorist attack on April 19, 1995, killing 168 people, also brought awareness to the dangers of AN.

Thermal decomposition of AN has been studied in literature using Differential Scanning Calorimetry (DSC) [12], Setaram C80 Heat Flux Calorimeter (C80) [13], Accelerating Rate Calorimetry (ARC) [14], Thermogravimetric Analysis (TGA) [15], and Adiabatic Dewar Calorimeter (ADC) [16]. Slight differences are found on data reported from the literature due to the variety of testing methods and equipment accuracy. The melting point of AN is around 170 °C and it decomposes above 210 °C [4]. Previous studies [17, 18] have reported that even at 200 °C, slow decomposition can occur. Adiabatic calorimetry tests of large samples of 100 g, indicate that AN may decompose as early as 190 °C [16].

Different decomposition mechanisms of AN have been reported in literature of which the most accepted reactions are summarized here [12, 15, 18-24]. An endothermic reversible reaction can occur at relatively low temperatures (i.e., around 170 °C). It is believed that the vaporization of melted AN leads to the formation of ammonia and nitric acid, which could initiate the decomposition of AN through the following reaction [12, 15, 18-22, 24].

\[
\text{NH}_4\text{NO}_3 \rightleftharpoons \text{HNO}_3 + \text{NH}_3, \quad \Delta H = 176 \text{ kJ mol}^{-1}
\]

At higher temperatures (i.e., between 170 °C and 280 °C) exothermic irreversible reactions occur [12, 15, 18-22, 24].

\[
\begin{align*}
\text{NH}_4\text{NO}_3 &\rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}, \quad \Delta H = -59 \text{ kJ mol}^{-1} \\
\text{NH}_4\text{NO}_3 &\rightarrow 1/2\text{N}_2 + \text{NO} + 2\text{H}_2\text{O}, \quad \Delta H = -257 \text{ kJ mol}^{-1} \\
\text{NH}_4\text{NO}_3 &\rightarrow 3/4\text{N}_2 + 1/2\text{NO}_2 + 2\text{H}_2\text{O}, \quad \Delta H = -944 \text{ kJ mol}^{-1}
\end{align*}
\]

If the material is suddenly heated up, there will be an explosive decomposition [21].

\[
\begin{align*}
2\text{NH}_4\text{NO}_3 &\rightarrow 2\text{N}_2\uparrow + \text{O}_2\uparrow + 4\text{H}_2\text{O} \quad \Delta H = -1057 \text{ kJ mol}^{-1} \\
8\text{NH}_4\text{NO}_3 &\rightarrow 5\text{N}_2\uparrow + 4\text{NO} + 2\text{NO}_2\uparrow + 16\text{H}_2\text{O} \quad \Delta H = -600 \text{ kJ mol}^{-1}
\end{align*}
\]

The explosion hazards of AN have been widely studied and a number of efforts have been made to study the thermal effects of AN with additives [10, 25-28]. The additives are classified into two types - promoters and inhibitors. Some chemicals behave as inert materials that result in the dilution of AN, or change the chemical reaction conditions due to incorporation, reducing the probability of an AN explosion [12]. These kind of chemicals are called inhibitors, which will help mitigate the AN explosion. Oxley et al. [12] have shown that the sodium, potassium, ammonium and calcium salts of sulfate, phosphate, or carbonate as well as certain high-nitrogen organics (urea, oxalate, formate, guanidinium salts) are good inhibitors as they enhance AN thermal stability and can be used as fertilizers. Sodium salts of weak acids (carbonic, acetic, formic, oxalic, and hydrofluoric) are also proven to be good inhibitors.
On the contrary, some other chemicals called promoters, accelerate the AN explosion rate. Promoters include explosive substances [3], such as nitrocellulose, aromatic nitro compounds; non-explosive combustible substances [3], such as sulphur, charcoal, flour, sugar, or oil; incombustible substances [3] such as pyrite [15], zinc, cadmium, and copper; chloride salts [13], such as ammonium chloride, barium chloride, calcium chloride, sodium chloride and potassium chloride; cations of chromium, iron and aluminum [17]; carbonaceous materials; hydrocarbon waxes [29]; inorganic acid, like sulfuric acid and hydrochloric acid [30]; common organic contaminants [2], such as animal fats, baled cotton, baled rags, baled scrap paper, bleaching powder, burlap of cotton bags, caustic soda, coke, charcoal, coal, cork, camphor, excelsior, fibers of any sort, fish oil, fish meal, foam rubber, hay, lubricating oil, fish meal, linseed oil or drying oils, naphthalene, oakum, oiled clothing, oiled paper, oiled textiles, paint, straw, sawdust, wood shavings and vegetable oil.

In this study, thermal decomposition of pure solid AN and its solution in water has been studied using a Reactive System Screening Tool (RSST) for the first time. The runaway behavior of AN has been characterized by obtaining important parameters like onset temperature, rate of temperature and pressure rise from the self-heating rate of AN. Further, the effects of two additives, sodium sulfate and potassium chloride, have been studied. Since the objective of this work is to study the effects of different types of additives on thermal decomposition of AN while maintaining its agricultural benefit, only inorganic salts that can be used as fertilizers have been chosen as additives for this study. Table 1 lists the nutrients most plants use in the form of fertilizers; the additives used in this work were selected from this list.

### Table 1. Nutrient content of plants [31, 32]

<table>
<thead>
<tr>
<th>Nutrition in air and water</th>
<th>6 Macronutrients</th>
<th>7 Micronutrients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>C</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>Phosphorus</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O</td>
<td>Potassium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calcium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iron</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Magnesium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Manganese</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulfur</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Molybdenum</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zinc</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nickel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cobalt</td>
</tr>
</tbody>
</table>

### 2. Experimental

#### 2.1. Chemicals

Ammonium nitrate (VWR Reagent, ACS Grade, 99.9% assay), Sodium sulfate (Aldrich, 99+% ACS Reagent), and Potassium chloride (Sigma, powder, Bio Reagent, 99.0+% assay) were used without further purification.
2.2. Reactive System Screening Tool (RSST™)

The RSST is a calorimeter manufactured by Fauske and Associates. It can screen reactive chemical systems for temperatures up to 500 °C and pressure up to 3549 kPa (490 psi). The RSST is capable of handling larger quantities of AN (approximately 3 g - 6 g) as compared to the Differential Scanning Calorimeter (DSC) which could use only several milligrams of sample. It is a pseudo-adiabatic calorimeter, which can compensate heat losses by adding additional energy generated from the heater. A sample is usually heated at a constant rate, which could vary from 0.25 °C min⁻¹ to 2 °C min⁻¹, attempting to simulate fire or explosion scenarios. This process is controlled by feedback from type K metal thermocouples. The sample self-heating rate of exothermic systems can be found as a function of sample temperature, which has been adjusted for heater input [33].

A schematic diagram of the RSST is shown in Figure 1.

![Figure 1. The schematic diagram of the RSST](image)

In a typical experiment, 3.5 g of powdered AN is weighed and loaded into the cell. To study the effect of different additives, 3.5 g of powdered AN is mixed well with 0.1 g of the additive in a solid form (AN mixture with 2.78 wt.% additive) and loaded into the cell. By comparing the data obtained for the mixture with pure AN data, it is easy to differentiate between the chemicals that mitigate the explosion (inhibitor) and those that intensify the explosion (promoter). In order to test the effect of mixing, a solution of AN is prepared by mixing 3.35 g of AN in 4.18 g of water (AN mixture with 55.5 wt.% water), which can fully dissolve AN. The molar ration of AN to water is 1:5.54.

Each test is repeated two to three times. The heating rate of 2 °C min⁻¹ was used for temperatures up to 150 °C; 1 °C min⁻¹ was used for temperatures from 150 °C to 180 °C; and 0.5 °C min⁻¹ was used for temperatures from 180 °C up to 340 °C. The shutdown temperature and pressure limit was 410 °C, and 400 psig, respectively. The initial backpressure of 187 psig is applied using a gas which is composed of 98.47% nitrogen and 1.53% oxygen. Parameters such as onset temperature, onset pressure, maximum temperature rate, maximum pressure rate, and temperature at maximum temperature rate are obtained from each experiment. Based on the results, the plots are drawn including temperature - time, pressure – time, log plot of self-heating rate - temperature and pressure rate - temperature.

3. Results and Discussion

3.1. Runway behavior of pure AN

In this section, the thermal decomposition of pure AN is described. In literature, AN has not been studied by RSST and this is the first study to report it. The temperature, temperature rate,
pressure, and pressure rate profiles are shown in Figure 2 for all the three repeating tests.

![Figure 2](image)

**Figure 2.** The thermal decomposition of AN. (a) Temperature profile (b) Self-heating rate (c) Pressure profile (d) Pressure rate

As can be seen from Figure 2, the three repeat tests for AN are not identical. In all the cases, the onset temperatures obtained are relatively close, around 200 °C, but the time to onset is different. The reason behind this could be that AN is tested in solid form and the RSST has only one thermocouple which is located at the center of the loaded cell. For solids, the heating rate and heat distribution within the sample might not be homogeneous. But the overall trends and critical parameters are almost the same.

When the temperature reaches around 200 °C, both the temperature and the pressure start to increase dramatically. This can be seen more clearly from the logarithmic plot of self-heating rate profile and pressure rate profile, which are shown in Figure 2 (b) and (d), respectively. From the results, the decomposition can be measured by the RSST at around 200 °C. The exothermic reaction starts very rapidly, generating gas and vapor accordingly.

In this paper, the onset temperature is defined from the self-heating rate profile. A tangent is drawn to the curve where the self-heating rate starts to increase, and then a straight line is drawn on the end of the temperature rate curve before the temperature starts to increase rapidly. The temperature at the intersection of these two lines is defined as the “onset” temperature. For neat AN, the onset temperature was determined to be 200 (±10) °C from the three repeat tests. The maximum temperature rate, \((dT/dt)_{\text{max}}\), is determined from the self-heating rate data, which is the maximum temperature rate recorded during the whole test process. In solid sample tests, the maximum temperature rate is reached before the shutdown of the experiment. \((dP/dt)_{\text{max}}\) is the maximum pressure rate determined in the same way. The temperature at maximum temperature rate, \(T_{\text{max}}\), is defined as the temperature when the maximum temperature rate occurs. From Figure 2, the maximum temperature rate is found to be 82 (±17) °C s\(^{-1}\), \(T_{\text{max}}\) occurred at 347 (±17) °C.

Oxley et al. [12] scanned neat AN using DSC at 20 °C min\(^{-1}\) from 50 °C to 450 °C. The results showed that there were two endotherms and one exotherm followed by another endotherm. The first endotherm happened at 125 °C and the second endotherm occurred at 169 °C due to the melting of AN. The exotherm was about 100 °C wide, with an exothermic maximum of 326 °C. In this work, the temperature at maximum temperature rate is observed at 347 (±17) °C which is comparable to their results. Sun et al. [30] has found that using DSC, in the exothermic peak, the heat flow increases very slowly and gradually with the temperature increasing in the range of 190–232 °C, and increases sharply above 232 °C. Similar behavior is observed in this work as well.
3.2. Effect of mixing
Here, the effect of mixing has been studied by making a solution of AN in water in the molar ratio of 1:5.5 (AN:water). Polymer coated magnetic stirrer bars were used in this test to make sure the solution is homogeneous. This will produce a more homogeneous sample, reducing the inhomogeneity caused by the neat solid. The temperature profile and temperature rate profile are shown in Figure 3. As can be seen from Figure 3 for the three repeating tests, two of the curves are identical and one of them still has a different time to onset. The temperatures at maximum temperature rate are almost the same. Also the standard deviation between maximum temperature rates is smaller than that of solid sample. The onset temperature is around 251 (±10) °C. The maximum temperature rate is 108 (±20) °C s⁻¹, which happened at 402 (±2) °C. It can be concluded from these results that there is no clear advantage of mixing AN with water to get repeatable times to onset. However, it can be seen that it delayed the onset temperature. This could happen because of many reasons and is a subject of a future study.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
</tr>
</tbody>
</table>

Figure 3. The thermal decomposition of AN with water. (a) Temperature profile (b) Self-heating rate

3.3. Effect of additives
The onset temperature of AN decomposition is around 200 °C as reported in section 3.1. When AN is mixed with additives, if the onset temperature is greater than 200 °C, the additive is defined as an inhibitor as it delays the onset temperature; if the onset is less than 200 °C, the additive is defined as a promoter as described below.

\[ T_{\text{onset}} = 200 \degree \text{C for AN} \]
\[ T_{\text{onset}} > 200 \degree \text{C} \text{ for inhibitors} \]
\[ T_{\text{onset}} < 200 \degree \text{C} \text{ for promoters} \]

3.3.1. Sodium Sulfate
In order to study the effect of additives, AN was mixed with 2.78 wt.% of sodium sulfate (Na₂SO₄) and the experiment was repeated two times. The temperature profile and the temperature rate profile are shown in Figure 4. Since the melting point of Na₂SO₄ is 884 °C, much higher than the temperature range of this research, there was residue remaining in the test cell after each test.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Charge ( U )</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(a)</td>
</tr>
</tbody>
</table>

Figure 4. The thermal decomposition of AN and Na₂SO₄. (a) Temperature profile (b) Self-heating rate

From Figure 4 (a), it can be seen that the temperature curve increases smoothly. As can be seen in Figure 4 (b), there is a slight difference (~16 °C) in the onset temperature for the two
repeating tests, but the temperatures at the maximum temperature rate are similar. The onset temperature is 250 (±11) °C, with the maximum temperature rate of 115 (±23) °C s⁻¹, which occurred at 383 (±4) °C.

On comparison of the results obtained for the mixture of AN with Na₂SO₄ against neat AN, it was found that the onset temperature increased by 50 °C and the temperature at maximum temperature rate increased by 36 °C. This shows that the addition of Na₂SO₄ delays the onset of runaway behavior of AN. As a conclusion, sodium sulfate is a good inhibitor for AN.

Similar results have been obtained using DSC [12] where Na₂SO₄ raised the decomposition exotherm of AN by 7 °C for AN mixture with 5 wt.% Na₂SO₄, and 23 °C for 20 wt.% Na₂SO₄.

3.3.2. Potassium Chloride
Another additive, potassium chloride (KCl), was used to study the runaway behavior of AN where 2.78 wt.% of KCl was mixed with AN. The temperature profile and temperature rate profile are shown in Figure 5. It can be seen from these figures that the presence of KCl tends to induce the thermal decomposition of AN earlier than pure AN. There is a slight difference for the two repeating tests. The onset temperature obtained is 188 (±11) °C, with the maximum temperature rate of 321 (±48) °C s⁻¹, which occurred at 287 (±23) °C.

On comparison of the results obtained for the mixture of AN with KCl, against neat AN, it was found that the onset temperature decreased by 12 °C and the temperature at maximum temperature rate decreased by 60 °C. The maximum temperature and pressure rate of AN with KCl also increases severely. This shows that the addition of KCl advances the onset of runaway behavior of AN and generates heat at a higher rate. As a conclusion, potassium chloride is a promoter for AN.

Other works in literature have shown that KCl has a strong promoter effect. Oxley et al. [12] found that KCl lowered the exotherm of AN by about 70 °C using DSC. Li and Koseki [13] found the exotherm was lowered by approximately 75 °C using C80, where samples of 500 mg were used.

![Figure 5](image-url)  
*Figure 5. The thermal decomposition of AN and KCl. (a) Temperature profile (b) Self-heating rate*

4. Conclusion
In this work, RSST has been used to study the runaway behavior of pure solid AN and AN solutions. The effects of additives, both inhibitors (sodium sulfate) and promoters (potassium chloride), have been studied. The decomposition behavior of AN is similar to the results reported in literature using DSC. It can be concluded that the presence of additives influences the onset temperature of AN decomposition. In the case of inhibitors, the onset temperature and
temperature at maximum temperature rate increase; whereas in the presence of promoters, these temperatures will decrease. The RSST used in this study is a screening tool which can give qualitative information about the rate of pressure increase, therefore, more work needs to be done in more precise instruments like adiabatic calorimeters to obtain quantitative and precise results.

References


http://ag.arizona.edu/pubs/garden/mg/botany/water.html - nutrition p. 34 - 38.


