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Calorimetry studies of ammonium nitrate – Effect of inhibitors, confinement, and heating rate

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ABSTRACT

Ammonium nitrate (AN) has been widely used as a fertilizer for almost a century because it is an excellent nitrogen source. However, AN related explosions continue to occur time and again, despite the fact that AN has been extensively investigated. There have been more than 70 AN-related incidents during the last century, which reemphasize the dire need for further research on AN reactive hazards. This research focuses on the alternatives to make AN safer as a fertilizer by reducing its explosivity, by studying the effect of inhibitors, confinement, and heating rate on AN thermal decomposition using the Reactive Systems Screening Tool (RSST). First, the thermal decomposition of AN in the presence of different types of additives, including sodium bicarbonate, potassium carbonate, and ammonium sulfate, was studied under two concentrations, *i.e.*, 2.8 wt.% and 12.5 wt.%. The results show that they are good inhibitors for AN. Second, the effect of confinement was tested by observing AN decomposition under five different initial pressures, varying from ambient pressure to 187 psig. It is concluded that confinement is dangerous to AN, which should be avoid in AN storage and transportation. Lastly, the effect of heating rate was studied by heating up AN under two heating rates of 0.25 °C min^{-1} and 2 °C min^{-1}. The lower the heating rate, the lower the "onset" temperature detected.

1. Introduction

Reactive chemicals are hazardous considering their tendency to result in runaway reactions. Ammonium nitrate (AN) in particular can lead to horrific explosions and fires. AN has caused a number of incidents during the last 100 years throughout the world, despite extensive past research on its properties and behavior, as well as current regulations on AN. Table 1 lists 77 AN-related incidents, out of which 41 occurred in the US. Only in the last three months of 2014, there have been three serious incidents related with AN around the world. On September 5, 2014, an AN truck explosion occurred in Australia (Atfield, 2014), injuring eight men including the driver, a police officer, and six firefighters (ABC, 2014). On November 6, 2014, a truck carrying AN caught fire near Kamloops, B.C., Canada (Petruk, 2014). On November 18, 2014, a trailer of AN caught fire at Ti Tree, Australia, and the trailer exploded after a while (Purtill and Liston, 2014).

AN has been used as a fertilizer for a long time. The annual consumption of AN in the US industry is millions of tons, among which around 20% is used as fertilizers and 80% is used as explosives or blasting agents (EPA, 2014). The US consumption of AN in 2011 was 0.7 million tons (FactFish). AN provides one of the most concentrated forms of nitrogen (35% N), and is referred to as AN-based fertilizer. AN accounts for more than 15% of the world's nitrogen fertilizer market (Lear, 2012). It is popular because it is very soluble in water, and hence is distributed very well in the soil, and the nitrate can move deep into the root zone of plants under wet conditions. Furthermore, AN and AN-based fertilizers are relatively inexpensive.

AN has a National Fire Protection Association (NFPA) instability/reactivity rating of 3, indicating that AN is capable of detonation, and explosive decomposition or reaction may occur. As a strong oxidizing agent, AN can detonate under certain conditions including the presence of impurities, confined spaces, and elevated temperature (EPA, 2014). The US Department of Transportation regulates AN with more than 0.2% combustible substances as an explosive material with specific storage requirements and restrictions in cargo vessels (EPA, 2014). This research discusses AN

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Table 1
AN related incidents (Guardian, 2013; Heather, 2002; Nygaard, 2006; Oxley et al., 2002; M. Wood and Duffield, 2002).

Location	Year	Location	Year
Kensington, UK	1896	Traskwood, AR, US	1963
Faversham, Kent, UK	1916	Typpi, Oy, Finland	1963
Oakdale, PA, US	1916	Mt. Vernon, MO, US	1966
Gibbstown, NJ, US	1916	Peytona, WV, US	1966
Morgan, NJ, US	1918	Amboy, IL, US	1966
Stolberg, Germany	1920	Potosi, WI, US	1967
Vergiati, Italy	1920	Taroom, Queensland, Australia	1972
Barksdale, WI, US	1920	France	1972
Brooklyn, NY, US	1920	Cheerokee, Prvor, OK, US	1973
Kriewald, Germany	1921	Bucharest, Romania	1974
Oppau, Germany	1921	Tahawas, NY, US	1976
Knurów, Poland	1921	Delaware City, DE, US	1977
Sinnnemahoning, PA, US	1922	Rocky Mountain, NC, US	1978
Cleveland, OH, US	1922	Moreland, ID, US	1979
Nixon, NewBrunswick, NJ, US	1924	UK	1982
Muscle Shoals, AL, US	1925	Kansas City, MO, US	1988
Emporium, PA, US	1925	Joplin, MO, US	1989
Gibbstown, NJ, US	1932	Porgera Valley, Papua New Guinea	1994
Merano, Italy	1936	Port Neal, IA, US	1994
Gibbstown, NJ, US	1940	Brazil	1997
Rouen, France	1940	Xingping, Shanxi, China	1998
Miramas, France	1940	Kentucky, US	1998
Tessenderloo, Belgium	1942	FL, US	2000
Milan, TN, US	1944	Toulouse, France	2001
Benson, AZ, US	1944	Cartagena, Murcia, Spain	2003
Texas City, TX, US	1947	Saint-Romain-en-Jarez, France	2003
Presque Isle, ME, US	1947	Keyshabur, Khorasan, Iran	2004
Brest, France	1947	Barracas, Spain	2004
St. Stephens, Canada	1947	Mihăileşti, Buzău, Romania	2004
Independence, KS, US	1949	Ryongchŏn, North Korea	2004
Pinole, CA, US	1953	Estaca de Bares, Spain	2007
Red Sea, Israel	1953	Monclova, Coahuila, Mexico	2007
Red Sea	1954	Bryan, TX, US	2009
New Castle, PA, US	1956	Zhaoxian, Hebei, China	2012
Mt. Braddock, PA, US	1958	West, TX, US	2013
Roseburg, OR, US	1959	Wyandra, Queensland, Australia	2014
Traskwood, AR, US	1960	B.C., Canada	2014
Boron, CA, US	1960	Ti Tree, Australia	2014
Norton, VA, US	1961		

decomposition in the presence of inhibitors, under confinement, and with various heating rates.

The thermal behavior of AN with various types of chemicals has been studied extensively. The presence of additives can greatly affect the decomposition of AN. Some chemicals, *i.e.* inhibitors, mitigate AN explosions when mixed with AN (Oxley et al., 2002). Most previous researches on AN with additives are studied using a Differential Scanning Calorimetry (DSC), which tests only a few milligrams of sample. When inhibitors are mixed with AN, they reduce the severity of AN decomposition by either acting as inert materials or changing the decomposition conditions and making it harder to occur. In this work, an inhibitor is defined as the chemical whose presence in the mixture with AN can increase its "onset" temperature. As reported in our previous work the "onset" temperature of pure AN in the Reactive System Screening Tool (RSST) is 200 °C (Han et al., 2015); therefore, an additive is considered as an inhibitor if when mixed with AN its decomposition "onset" temperature becomes higher than 200 °C. In order to mitigate AN hazards, inhibitors are mixed with AN to reduce its explosivity. Since AN is used as fertilizer, such additives should be ideally beneficial, or at least not harmful to crops. This work reports the findings of the effect of inhibitors, including sodium bicarbonate, potassium carbonate, and ammonium sulfate. All of the three selected additives are commercial fertilizers (Munns, 1965; Nalewaja et al., 1989; Patnaik, 2002), and they have never been studied systematically. Existing studies with DSC, which is essentially a screening only tool cannot be as reliable as the present study with RSST, which employed a few grams of sample.

Confinement also plays an important role in AN decomposition. All three previously stated incidents in 2014 occurred during transportation, and in a confined space. Confinement was also believed to help trigger the explosion in the Port Neal plant incident (Shockey et al., 2003; Thomas et al., 1996). The European Fertilizer Manufacturers Association's (EFMA) guidance document states that AN has high resistance to detonation; however, heating under strong confinement can lead to explosive behavior (EFMA, 2005). According to NFPA 49, if AN is heated under confinement causing a pressure build-up, it may undergo detonation (Spencer and Colonna, 2002). Accelerating Rate Calorimeter (ARC) has been used to study the runaway behavior of nitroguanidine to observe the effects of confinement (Lee and Back, 1988) by comparing its decomposition in both confined and non-confined system. The results show that in the confined system, the "onset" temperature of nitroguanidine decomposition is lower than that of the non-confined system, the self-heating rate is faster, the time to maximum rate is shorter, and the rate of pressure increase is faster. However, the effect of confinement on AN has not been reported in literature. Therefore, such experiments need to be performed on AN to study the effect of confinement and identify similarities or difference with the reactive behavior of other nitro–compounds. In view of this, one of the targets of this work is to study the effect of confinement on AN decomposition using a similar strategy to the one used by Lee and Back (1988), *i.e.* by varying the initial pressures of N_2 gas. By understanding the risks of confined space, this study