MARY KAY O'CONNOR PROCESS SAFETY CENTER
TEXAS A&M ENGINEERING EXPERIMENT STATION

20th Annual International Symposium
October 24-26, 2017 • College Station, Texas

Prediction of NH_4NO_3 thermal decomposition parameters in the presence of two additives using the single additive experimental values

Zhe Han[1], Sonny Sancheva[1], **Maria Papadaki[2*]** and Sam Mannan[1*]
1. Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843-3122, USA
2. Department of Environmental & Natural Resources Management, School of Engineering, University of Patras, SEFERI 2, AGRINIO, GR30100, GREECE
* Presenter e-mail:marpapadaki@upatras.gr

Abstract

NH_4NO_3 thermal decomposition rate is significantly affected by the presence of additives such as Na_2SO_4 (an inhibitor) or KCl (a promoter). The presence of Na_2SO_4 increases substantially the decomposition "onset" temperature of NH_4NO_3; K_2CO_3 does the same, while KCl reduces the same parameter. In this work the effect of individual additives on characteristic thermal decomposition parameters of NH_4NO_3 have been correlated and used to predict the respective parameters when two additives are present simultaneously. A simple model predicting the effect of mixtures of additives on the "onset" temperature and the temperature rise due to the thermal decomposition of AN, using the same data from the individual compounds was developed. The results showed that the behavior of each compound is independent from that of the others. The model predicts well T_o and T_f of such mixtures of additives.

Introduction

Ammonium nitrate (AN) is used as an explosive and a fertilizer. US industry uses of millions of tons on an annual basis, among which around 20% is used as fertilizers and 80% is used as explosives or blasting agents [1] 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 [2]. 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 is not considered as a dangerous material at atmospheric conditions [3,4], but it is a strong oxidizing agent that can result in incidents [5, 6]. A number of incidents have occurred due to the detonability of AN, which has caused extensive loss of property and life. One recent incident is the explosion in West, Texas, which killed 15 people and injured more than 250 people. Despite

considerable research performed on understanding the detonability of AN, incidents like West, Texas, are still happening, and this calls for gaining even deeper understanding of the underlying causes of its unpredictable behavior at times. AN has an 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 [1]. 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 [1].

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 [7]. 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 make 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 [8]; therefore when an additive is considered as an inhibitor if when mixed with AN, increases its decomposition "onset" temperature to values higher than 200 °C. In order to mitigate AN hazards, inhibitors are mixed with AN to reduce explosivity. Since AN is used as fertilizer, such additives should be ideally beneficial to plants, or at least they will not harm the crop. Different compounds act as promoters of the decomposition, reducing the "onset" temperature and/or the generated heat.

This work combines the findings of the effect of inhibitors, including sodium sulphate, potassium carbonate, and potassium chloride. All these additives are commercial fertilizers. As such, if they act as inhibitors, it may be beneficial to be added to the fertilizer from a safety point of view. On the other hand, if they act as promoters, their removal will not be beneficial for the crops. However, synergistic effects with inhibitors can make the fertilizer safer, so the effects of mixtures of additives is a simple method to produce a safer fertilizer.

Experimental research conducted in MKO Process Safety Center, focused on the effects that certain additives and conditions had on AN thermal decomposition, using the ARSST and APTAC. [8,9,10]. This research quantified the effect which Na_2SO_4, K_2CO_3 and KCl had on common parameters used in safety evaluations. It was found that the former two additives with fertilizing potential, act as inhibitors of the AN thermal decomposition, while the later acts as a thermal decomposition promoter. It was found that with more Na_2SO_4 in the mixture, the "onset" temperature increases and the maximum self-heating rate decreases, showing that Na_2SO_4 is a good inhibitor for AN. On the other hand, the presence of KCl substantially decreases the "onset" temperature of AN. It was observed that the lowering of the "onset" temperature owing to the addition of KCl was changed linearly with KCl quantity. On the other hand, the effect of Na_2SO_4 addition on the "onset" temperature rise showed a linear dependence on quantity, only for small quantities (less than 0.5 g of Na_2SO_4 in 3.5 g of AN) of the additive and became insensitive at higher concentrations.

Research was also conducted employing mixtures of the above additives. In the present work, the effects which individual additives had on the adiabatic temperature rise and the temperature at

maximum rate were correlated and used for the prediction of the effect which mixtures of these additives had on the respective parameters. The results were then compared with the experimental ones.

Experimental

Chemicals

Ammonium nitrate (NH_4NO_3, VWR Reagent, ACS Grade, 99.9% assay), potassium carbonate (K_2CO_3, Mallinckrodt, ACS Grade), Sodium sulfate (Aldrich, 99%, ACS Reagent), and Potassium chloride (KCl, Sigma, powder, Bio Reagent, 99.0%) were used without further purification.

The experimental procedure followed is described in detail in our previous work. [8]. In all measurements used in this paper 3.5 g of ammonium nitrate was employed.

Results and Discussion

Table 1. Experimental measurements employing 3.5 g of ammonium nitrate and each individual additive shown.

Additive mass (g)	Additive number of mole	Additive mol-fraction	Experimental parameters				
			T_f	T_o	T_{max}	$\Delta T_{contr,1}$	$\Delta T_{contr,2}$
SODIUM SULFATE							
0	0	0	393	200	347		0
0.04	0.000282	0.0064	441	240	394	1	8
0.06	0.000422	0.0096	438	248	387	-10	-3
0.1	0.000704	0.0159	423	250	381	-27	-20
0.2	0.001408	0.0312	429	255	392	-26	-19
0.3	0.002112	0.0461	423	260	377	-37	-30
0.4	0.002816	0.0605	420	263	379	-43	-36
POTASSIUM CARBONATE							
0	0	0	393	200	347	-7	
0.1	0.001341	0.0298	457	260	414	-3	
0.1869	0.002507	0.0542	452	263	387	-11	
0.3857	0.005174	0.1058	448	276	400	-28	
0.5976	0.008016	0.1549	440	275	395	-35	
0.8240	0.011053	0.2018	440	275	400	-35	
POTASSIUM CHLORIDE							
0	0	0	393	200	347	-7	
0.1	0.001341	0.0298	427	194	301	33	
0.2	0.002683	0.0578	398	196	323	2	
0.3	0.004024	0.0842	408	196	309	12	
0.45	0.006036	0.1213	446	180	292	66	
0.5	0.006707	0.1330	453	152	295	101	

1.0	0.013414	0.2348	468	145	302	123	

Table 1 shows the measurements employing pure additives. The data of those measurements were used for the correlation. In safety studies, quantities are usually expressed in mass units; however, to address issues related with chemical reactions, molar quantities are more meaningful, thus such measures of mass have been used in the correlations.

The first column of Table 1 shows the mass of the additive employed, the second its number of moles and the third its mole-fraction in the mixture. The three subsequent columns show the final temperature, T_f, the "onset" temperature, T_o and the temperature of the mixture, T_{max}, at the maximum rate, respectively. In the last two columns an effective contribution, ΔT_{contr} of the additive in the temperature rise is shown. In the one but the last column, this contribution is expressed as $(T_f-T_o)-T_{o,pureAN}$ of pure ammonium nitrate. In the last column, this contribution is expressed as $(T_f-T_o)-(T_f-T_o)_{pureAN}$ of pure ammonium nitrate. Adiabatic temperature rise (Tf – To) is closely related with the heat of reaction. As shown in our previous studies [8,9,10], the studied inhibitors and promoters had an effect on the generated heat of reaction, which subsequently affected the T_f. As such, the prediction of T_f corresponds to prediction of the change in the heat of reaction.

The contributions were correlated as linear relations and the linear fit for each case is shown in Figures 1 and 2. On each figure the slope of the respective straight line is shown. The R^2 of each fit, too.

Table 2 shows the measurements obtained from mixtures of additives and the predicted temperature rise using each correlation. The calculation of the adiabatic temperature rise when using the formula of the effective contribution 1, was done as follows:

Table 2. Experimetal parameters of measurements with mixtures

mole fractions			Experimental parameters				
Na_2SO_4	K_2CO_3	KCl	To	T_{max}	T_f	$(T_f-T_o)-T_{o,pureAN}$	$(T_f-T_o)-(T_f-T_o)_{pureAN}$
0.01	0.01	0.01	221	332	452	31	38
0.02	0.02	0.02	234	339	443	9	16
0.03	0.03	0.03	245	313	459	14	21
0.037	0	0.037	231	317	450	19	26
0.036	0	0.069	231	335	478	47	54
0.065	0	0.124	237	343	490	53	60
0.069	0	0.069	240	340	470	30	37

$$(T_f-T_o)_{predicted}=(T_o)_{pureAN}+\Delta T_{effSS}+\Delta T_{effPC}+\Delta T_{effKCl} \quad (1)$$

and

$$T_f=(T_f-T_o)_{predicted}+T_{o,pureAN} \quad (2)$$

Where ΔT_{effSS}, ΔT_{effPC}, ΔT_{effKCl}, are the effective contribution (1) of sodium sulphate (SS), potassium carbonate (PC) and potassium chloride KCl, respectively.

The calculation of the adiabatic temperature rise when using the formula of the effective contribution 2, was done as follows:

$$(T_f-T_o)_{predicted}=(T_f-T_o)_{pureAN}+\Delta T_{effSS}+\Delta T_{effPC}+\Delta T_{effKCl} \quad (3)$$

Where ΔT_{effSS}, ΔT_{effPC}, ΔT_{effKCl}, are the effective contribution (2) of sodium sulphate (SS), potassium carbonate (PC) and potassium chloride KCl, respectively

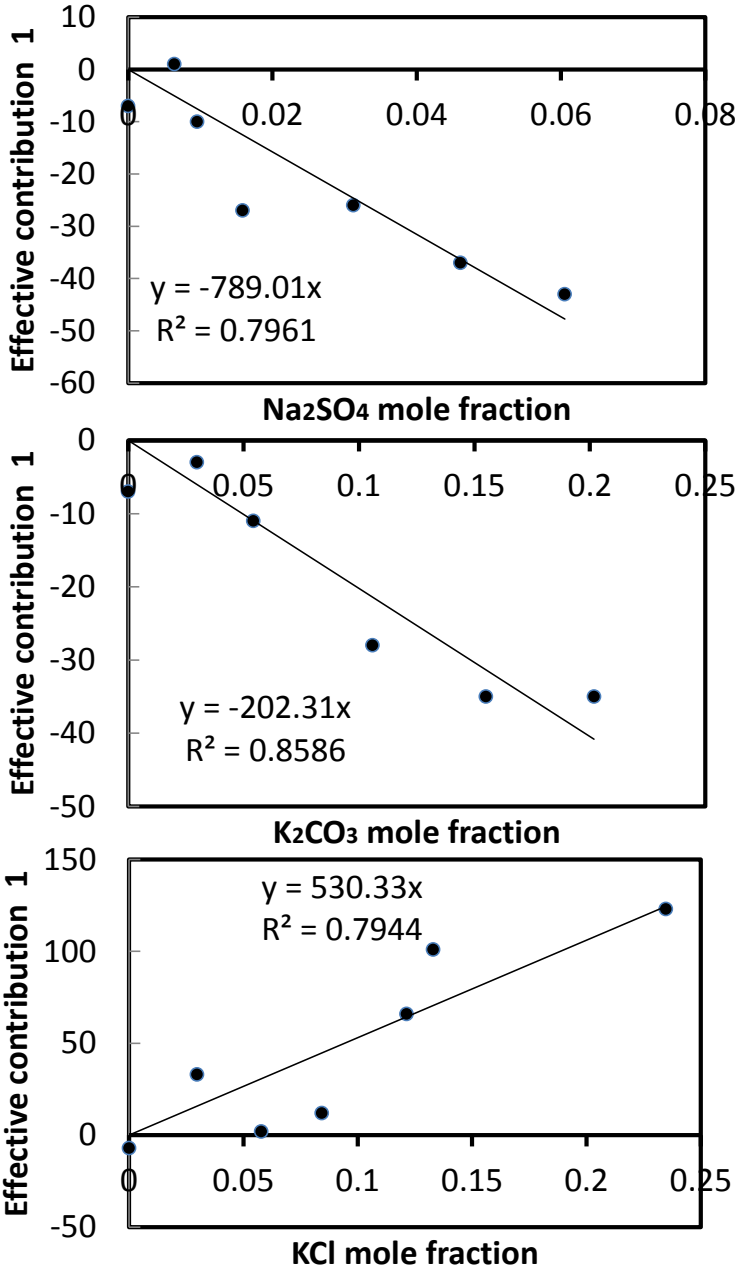

Figure 1.Effective contribution of each additive to the adiabatic temperature rise expressed as (T_f-T_o)-$(T_o)_{pureAN}$.

The adiabatic temperature at maximum rate –to be shown in the presentation-was also calculated using the same kind of correlations.

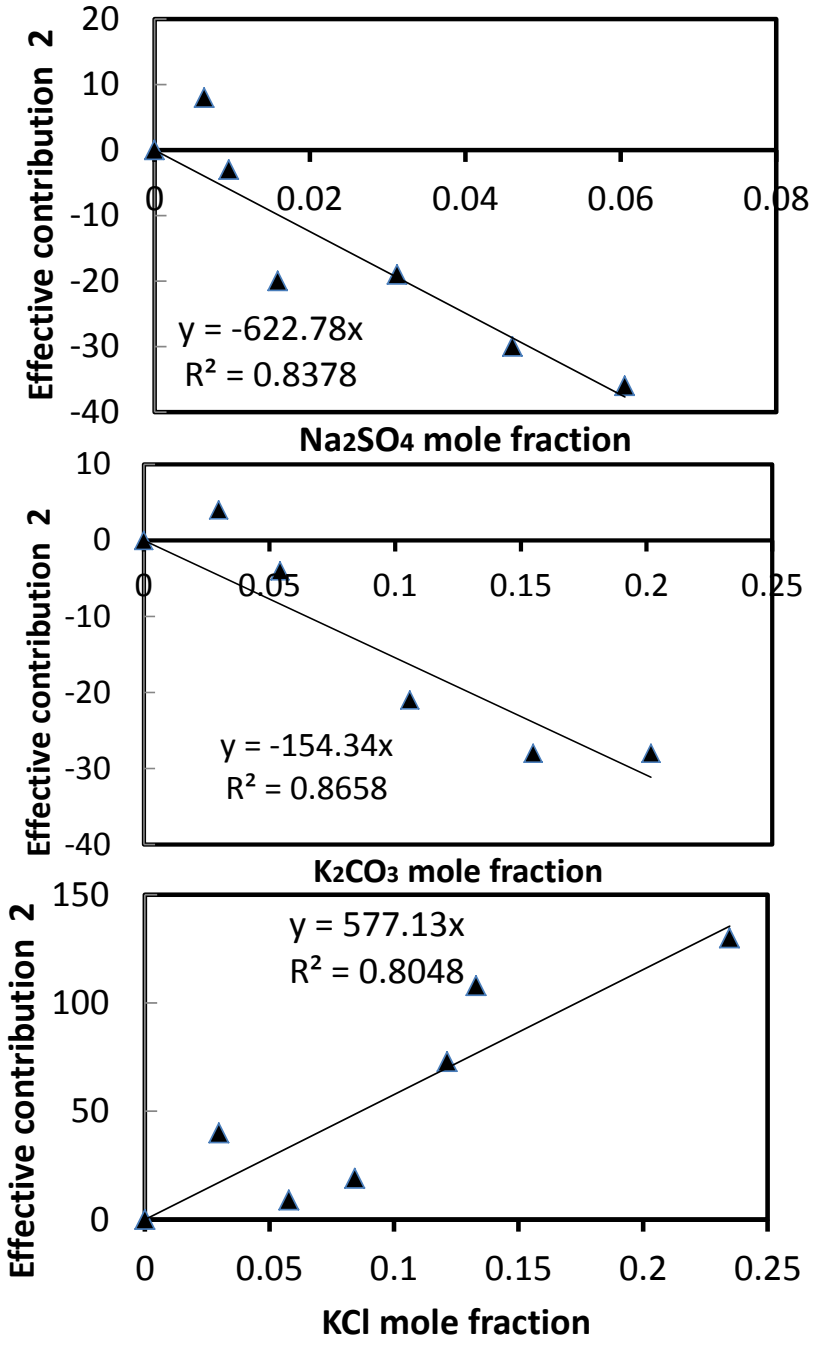

Figure 2.Effective contribution of each additive to the adiabatic temperature rise, expressed as $(T_f-T_o)-(T_f-T_o)_{pureAN}$.

Table 3. Comparison of experimental and predicted temperature rise for mixtures of additives.

Effective contribution calculation as $(T_f-T_o)-(T_f-T_o)_{pureAN}$

Contributions

Na_2SO_4	K_2CO_3	KCl	Sum of contributions	$(T_f-T_o)_{pred}$	$(T_f-T_o)_{exp}$	**% dev**	T_f-pred	T_{f_exp}	**% dev**
-6.23	-1.54	5.77	-2.00	191.00	231	**-17.32**	391.00	452	**13.50**
-12.46	-3.09	11.54	-4.00	189.00	209	**-9.57**	389.00	443	**12.19**
-18.68	-4.63	17.31	-6.00	187.00	214	**-12.62**	387.00	459	**15.69**
-23.21	0.00	21.31	-1.90	191.10	219	**-12.74**	391.10	450	**13.09**
-22.45	0.00	39.63	17.18	210.18	247	**-14.91**	410.18	478	**14.19**
-40.64	0.00	71.75	31.11	224.11	253	**-11.42**	424.11	490	**13.45**
-43.22	0.00	39.68	-3.54	189.46	230	**-17.63**	389.46	470	**17.14**

Effective contribution calculation as $(T_f-T_o)-(T_o)_{pureAN}$

Na_2SO_4	K_2CO_3	KCl	sum	T_f-pred	T_{f_exp}	% dev
-7.89	-2.02	5.30	-4.61	395.39	452	**12.52**
-15.78	-4.05	10.61	-9.22	390.78	443	**11.79**
-23.67	-6.07	15.91	-13.83	386.17	459	**15.87**
-29.41	0.00	19.58	-9.82	390.18	450	**13.29**
-28.44	0.00	36.42	7.98	407.98	478	**14.65**
-51.48	0.00	65.93	14.45	414.45	490	**15.42**
-54.75	0.00	36.46	-18.29	381.71	470	**18.79**

The results show that the presence of Na_2SO_4 and KCl together increased the "onset" temperature of AN, which lowered the possibility of AN decomposition. However, it also increased the maximum temperature, which increases the consequences of AN decomposition should it occur. When in isolation, Na_2SO_4 increases T_o and reduces the adiabatic temperature rise $(T_f - T_o)$. On the other hand, KCl alone reduces T_o while it has a significant effect on the values of all other parameters, which increase.

The deviations of the predicted from the experimental values were within the experimental error of the original data employed, thus showing a promising potential. Further work is planned.

Conclusions

A simple model predicting the effect of mixtures of additives on the "onset" temperature and the temperature rise due to the thermal decomposition of AN, using the same data from the individual compounds was developed. The results showed that the behavior of each compound is independent from that of the others.

References

1 EPA, 2014. Request for Information: Accidental Release Prevention Requirements:Risk Management Programs under the Clean Air Act. Section 112®(7). Federal Register The daily journal of the United States Government: Environmental Protection Agency. 40 CFR Part 68.

2 Lear, H., 2012. Ammonium Nitrate Outlook 2012 from Affinity. The Noble Metals N_2O abatement and related products newsletter. http://www.noble.matthey.com/affinity/issue3/ano.htm.

3. Texas, *Texas City, Texas, Disaster, April 16, 17, 1947*. 1947, Fire Prevention and Engineering Bureau of Texas, Dallas, Texas; The National Board of Fire Underwriters, New York, New York.: http://www.local1259iaff.org/report.htm.

4. Marlair, G. and Kordek, M.-A., *Safety and security issues relating to low capacity storage of AN-based fertilizers.* Journal of Hazardous Materials, 2005. **123**(1–3): p. 13-28.

5. HSE, *Storing and handling ammonnium nitrate*. 1996: http://www.hse.gov.uk/pubns/indg230.pdf.

6. EPA, *Explosion hazard from ammonium nitrate*. 1997, Chemical Emergency Preparedness and Prevention Office: http://www.epa.gov/osweroe1/docs/chem/ammonitr.pdf.

7 Oxley, J.C., Smith, J.L., Rogers, E., Yu, M., 2002. Ammonium nitrate: thermal stabilityand explosivity modifiers. Thermochim. Acta 384 (1-2), 23-45.

8 Z. Han, S. Sachdeva, M. I. Papadaki, M. S. Mannan, Ammonium nitrate thermal decomposition with additives, Journal of Loss Prevention in the Process Industries 35 (2015) 307-315.

9. Z. Han, S. Sachdeva, M. I. Papadaki, M. S. Mannan, Calorimetry studies of ammonium nitrate: Effect of inhibitors, confinement, and heating rate, Journal of Loss Prevention in the Process Industries 38 (2015) 234-242,

10. Z. Han, S. Sachdeva, M. I. Papadaki, M. S. Mannan,Effects of inhibitor and promoter mixtures on ammonium nitratefertilizer explosion hazards Thermochimica Acta 624 (2016) 69–75