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Thermal stability and kinetics of decomposition of ammonium nitrate in the presence of pyrite

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ABSTRACT

The interaction between ammonium nitrate based industrial explosives and pyrite-rich minerals in mining operations can lead to the occurrence of spontaneous explosion of the explosives. In an effort to provide a scientific basis for safe applications of industrial explosives in reactive mining grounds containing pyrite, ammonium nitrate decomposition, with and without the presence of pyrite, was studied using a simultaneous Differential Scanning Calorimetry and Thermogravimetric Analyser (DSC–TGA) and a gas-sealed isothermal reactor, respectively. The activation energy and the pre-exponential factor of ammonium nitrate decomposition were determined to be 102.6 kJ mol^{-1} and 4.55×10^7 s^{-1} without the presence of pyrite and 101.8 kJ mol^{-1} and 2.57×10^9 s^{-1} with the presence of pyrite. The kinetics of ammonium nitrate decomposition was then used to calculate the critical temperatures for ammonium nitrate decomposition with and without the presence of pyrite, based on the Frank–Kamenetskii model of thermal explosion. It was shown that the presence of pyrite reduces the temperature for, and accelerates the rate of, decomposition of ammonium nitrate. It was further shown that pyrite can significantly reduce the critical temperature of ammonium nitrate decomposition, causing undesired premature detonation of the explosives. The critical temperature also decreases with increasing diameter of the blast holes charged with the explosive. The concept of using the critical temperature as indication of the thermal stability of the explosives to evaluate the risk of spontaneous explosion was verified in the gas-sealed isothermal reactor experiments.

1. Introduction

Ammonium nitrate and fuel oil mixture (ANFO), an industrial explosive commonly used in open-cut mining operations, when in direct contact with pyrite may spontaneously detonate, potentially causing loss of life, property and productivity. This is termed spontaneous explosion and has been believed to be due to the complex reactions between ammonium nitrate and the pyrite or the products from the low temperature oxidation of the shale when the shale is exposed to the ambient air and moisture (weathering) [1]. There have been numerous reported incidents of spontaneous explosions in many mines around the world, for instance Mt Isa copper mine and Mt Whaleback iron ore mine in Australia [2,3], Dexing, Dongxiang, Pingshui, and Wushan copper mines, Xingqiao and Jurong pyrite ore mines, and Dachang tin ore mine in China [4], Lihir gold mine in Papua New Guinea [5], Mt Con copper mine and Meikle gold mine in USA [6,7], and Mt Con gold mine in Canada [8].

In a detailed multi-stage mechanism proposed by Rumball [1], ammonium nitrate reacts with sulphuric acid and ferrous ions from pyrite oxidation to generate nitrous acid. The nitrous acid then further reacts with pyrite in an intermediate stage, which is highly exothermic and produces NO_x. The NO_x produced then catalyses the decomposition of ammonium nitrate, leading to thermal runaway [9].

It is known that the decomposition temperature of pure ammonium nitrate is relatively high (170 °C) [10], yet spontaneous explosion of ANFO as a result of its interaction with pyrite can occur at temperatures as low as 25–50 °C [1,11]. Therefore, it is suspected that the thermal stability of ammonium nitrate is significantly reduced when in contact with pyrite so that ammonium nitrate may be decomposed at much lower temperatures. However this aspect has been overlooked in the literature.

The mechanism of ammonium nitrate decomposition has been a focus of several studies in the literature [12–14]. Several mechanisms have been proposed, since the observed thermolysis of ammonium nitrate is greatly dependent on the experimental conditions, including pressure, temperature, sample size, state of confinement, heating rate, time lapsed in monitoring the gaseous

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product, and the presence of trace amounts of impurities or additives. The dependence of the thermolysis on these factors is so significant that an endothermic process can be transformed to an exothermic process simply by varying the sample size, pressure or the state of confinement [14].

During the decomposition of ammonium nitrate by applying heat, four chemical species (NH_3, HNO_3, N_2O and H_2O) are formed in the gas phase, as shown in reactions (1) and (2). If these gases are evacuated and rapidly cooled as they are released from the system (for example, by heating a small size of ammonium nitrate in an open system), the gaseous product will only be the four chemical gases as quoted above and the decomposition process is observed as endothermic. However, if the aforementioned gases are maintained at the temperature at which they are formed (for example, by heating ammonium nitrate in a closed container or a large amount of ammonium nitrate where the gaseous products will be trapped in the void fraction between particles), these gases may further react with one another to form water, nitrogen, and nitric oxide, and the complete decomposition process is observed as exothermic process [15].

Nevertheless, it is widely accepted that the thermal decomposition of ammonium nitrate is initiated by the vaporization of melted ammonium nitrate accompanied by a proton transfer reaction leading to the formation of ammonia and nitric acid, as shown in reaction (1) [12].

$$NH_4NO_{3(l)} \leftrightarrow NH_{3(g)} + HNO_{3(g)}, \quad \Delta H = 176\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

The reversible reaction (1) emphasizes that the vapors of nitric acid and ammonia are able to recombine to form ammonium nitrate crystals on a cold surface. In addition, ammonium nitrate was also detected in the gas phase as a result of the recombination of $HNO_{3(g)}$ and $NH_{3(g)}$ [16].

As temperature increases to above 170 °C, ammonium nitrate begins to decompose irreversibly into water and nitrous oxide according to the following reaction [17]:

$$NH_4NO_{3(l)} \rightarrow N_2O_{(g)} + 2H_2O_{(g)}, \quad \Delta H = -59\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

Reactions (1) and (2) occur simultaneously. The detailed transition pathways from reactions (1) to (2) have been the subject of extensive research [12–14].

On the other hand, the kinetics of the thermal decomposition of ammonium nitrate has also been extensively studied, using a variety of techniques under different experimental conditions [12,13,18–27], but the results reported in the literature are inconsistent and inconclusive. For example, the reported activation energy for ammonium nitrate decomposition varies from 86.2 to 206.9 $\mathrm{kJ\,mol^{-1}}$. However, all the previous researchers in this area agree that the overall decomposition reaction of ammonium nitrate is described by the first order reaction kinetics.

As discussed before, the occurrence of spontaneous explosion could be due to the loss of *thermal stability* of ammonium nitrate, as a main ingredient in ANFO, when brought into contact with the pyrite. One of the most important parameters for the *thermal stability* of explosives is the critical temperature under a given set of conditions. The critical temperature is defined as the lowest constant surface temperature at which a specific material with a given size and shape will self-heat auto-thermally. However, the critical temperature for ammonium nitrate decomposition has not been determined and reported before.

The present study aims to obtain the critical temperature of ammonium nitrate decomposition, as an indication of the thermal stability of ANFO that can be used to evaluate the risk of spontaneous explosion. In order to determine the critical temperature of ammonium nitrate decomposition, it is necessary to obtain the kinetics of ammonium nitrate decomposition, with and without the presence of pyrite. In determining the kinetics of ammonium nitrate decomposition, various important factors that were overlooked by previous researchers, such as sample mass, reaction atmosphere and heating rate will also be examined.

2. Experimental

In order to achieve the above objectives, kinetic parameters (activation energy and pre-exponential factor) of ammonium nitrate decomposition with and without pyrite were obtained using thermal analysis techniques. The kinetics was then used to calculate the critical temperatures for ammonium nitrate decomposition with and without the presence of pyrite and subsequently verified against experimental results using an isothermal reactor technique at a larger sample size.

The pyrite used in this study was collected from an iron ore mine in northern Western Australia. They were pyrite nodules originally embedded in the overburden or interburden waste rocks and were of spherical/oval shapes with a mean diameter of approximately 20 mm. These pyrite nodules were then separated from the original rock by crushing using a jaw crusher. The separated nodules

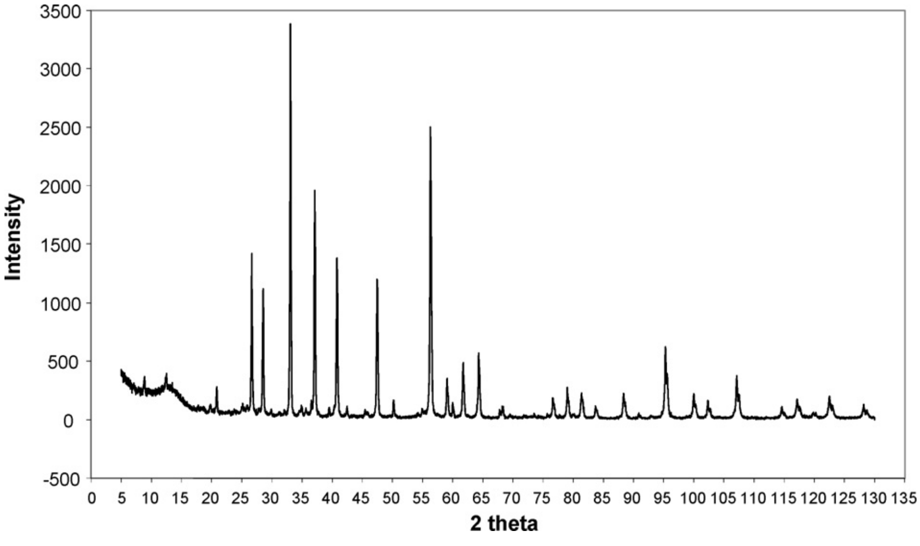

Fig. 1. XRD spectra of the pyrite.

were then pulverised to below 100 μm. Quantitative XRD analysis showed the purity of the pyrite was above 93.5% and the impurities included Quartz, Muscovite, Hematite, Birnessite and Fraipontite. Fig. 1 shows the XRD spectra of the pyrite used in this study. This pyrite has been known to readily react with ANFO, incurring spontaneous combustion when exposed to air and generate acid run-off in the waste dumps and, therefore, is an ideal pyrite for this study of its effect on the stability of ammonium nitrate.

A simultaneous DSC–TGA (TA Instrument Q600) was used to study the kinetics of ammonium nitrate decomposition with and without pyrite. Analytical grade ammonium nitrate in the form of powder sourced from Mallinckrodt Baker was used in the experimentation. Air, nitrogen and argon gases of industrial grade were employed as the gas media. Temperature calibrations for both DSC and TGA modules were performed in the range 298–873 K by running melting standards including Indium, Tin and Lead (purity: 99.9%). Blank runs were conducted under the same conditions with an empty 90 μL (ID = 5 mm) alumina crucible to obtain baselines for different heating rates. These baselines were subtracted from the mass loss curves with samples in the crucibles and the resulting curves were considered the actual mass change curves and were used for further analysis. For the kinetic studies of ammonium nitrate decomposition, various amounts of powdered ammonium nitrate (0.5–50 mg) were decomposed in a non-isothermal mode with various constant heating rates (1, 5, 10, 20 and 50 K min^{-1}, respectively), from room temperature to 400 °C.

A gas-sealed isothermal reactor system as schematically shown in Fig. 2 was used to provide a quantitative indication of gaseous products during ammonium nitrate decomposition with and without the pyrite and to verify the critical temperature to be predicted from the kinetic parameters obtained in this study. The isothermal reactor is made of pyrex with internal diameter of 21 mm and height of 200 mm. Temperature inside the reactor was monitored with a thermocouple inserted into the mixture of pyrite and ammonium nitrate. Argon was used to purge the reactor and to dilute and carry the product gases to the analytical instrument. Enerac 3000 gas analyser was used to analyse for NO, NO_2, NO_x, CO, CO_2, SO_2, and O_2 in the gas produced and recorded every minute. The gas composition and temperature data were recorded on a computer.

3. Theory and analysis

When ANFO is charged into a blast hole with known size and shape in a mining ground, the critical temperature specifies the lowest surrounding ground temperature at which the ammonium nitrate will self-heat and lead to a spontaneous explosion. According to Luo et al. [28], the critical temperature, T_c, may be calculated from Eq. (3) for an infinite cylinder, which is derived from the Frank–Kamenetskii theory of thermal explosion.

$$\frac{E}{RT_c} = 4.72918 + \frac{1.04565\,\ln RQAr_0^2}{E\lambda} \tag{3}$$

where r_0 is the radius of the cylinder (m), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), λ is the thermal conductivity of the material (W m^{-1} K^{-1}), Q is the heat of reaction (J m^{-3}), E and A are the activation energy (J mol^{-1}) and pre-exponential factor (s^{-1}) of the reaction, respectively. It is clear that the critical temperature is a function of E, A, and r_0.

Thus, the kinetics of ammonium nitrate decomposition needs to be determined. The kinetics of the ammonium nitrate decomposition with and without presence of pyritic black shale can be determined using the Kissinger method [29], which uses the temperature (T_m) at which the reaction rate is at a maximum as obtained from the DSC curves of ammonium nitrate decomposition in experiments using different heating rates. The equation is as follows.

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \tag{4}$$

where β is the heating rate (K min^{-1}). The slope and intercept from the line plot of $\ln(\beta/T_m^2)$ against $1/T_m$ are used to obtain the activation energy and pre-exponential factor, respectively [29].

4. Results and discussion

4.1. Decomposition of pure ammonium nitrate

Fig. 3 shows typical DSC–TGA curves for pure ammonium nitrate over the temperature range from 25 to 350 °C, within which several thermal events occur. From the DSC curve, four endothermic peaks can be identified during the course of the heating of ammonium nitrate. The first two endothermic peaks occur at ~50 and ~127 °C due to the crystallographic transformation IV → II and II → I, respectively [30]. The crystallographic data of the observed phases of ammonium nitrate are detailed in Table 1. The third endothermic peak, corresponding to the melting point of ammonium nitrate, occurs near 170 °C, after which the decomposition starts. The fourth peak, corresponding to the maximum rate of decomposition, is reached at approximately 290 °C. The TGA curve shown in Fig. 3 confirms that the decomposition of ammonium nitrate is the major cause of mass loss.

The effect of sample mass on the DSC–TGA curves of ammonium nitrate decomposition was investigated in air and it was found that the sample mass has a significant effect on the rate of ammonium

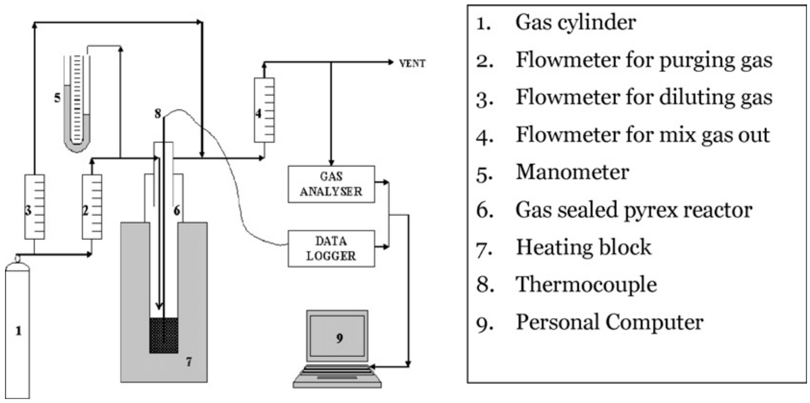

Fig. 2. A schematic of the isothermal gas-sealed reactor system.

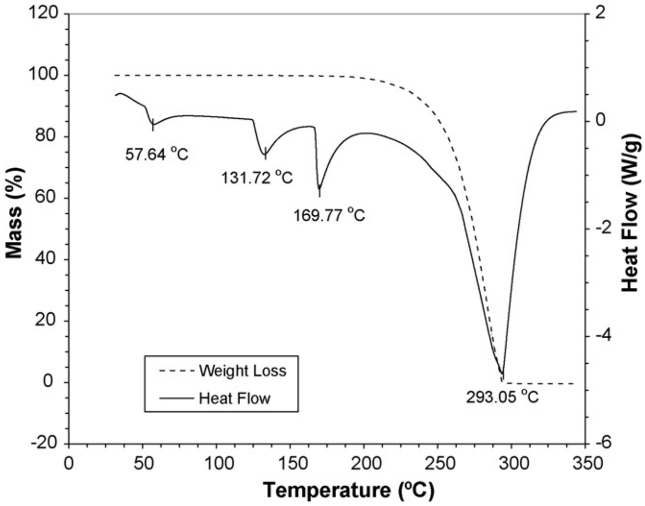

Fig. 3. Typical mass loss and heat flow curves of ammonium nitrate decomposition in air in the DSC–TGA experiments.

Table 1
Crystallographic information of the observed phases of ammonium nitrate [30].

Phase	Temperature region (°C)	Symmetry, *Z*	Lattice constants (Å)
NH_4NO_3 (I)	125–170	Cubic, *Z* = 1	*a* = 4.37
NH_4NO_3 (II)	84–125	Tetragonal, *Z* = 2	*a* = 5.7193, *c* = 4.9326
NH_4NO_3 (IV)	−18–32	Orthorhombic, *Z* = 2	*a* = 5.745, *b* = 5.438, *c* = 4.942

nitrate decomposition, as shown in Figs. 4 and 5. The sample mass was varied from 1.63 to 52.66 mg.

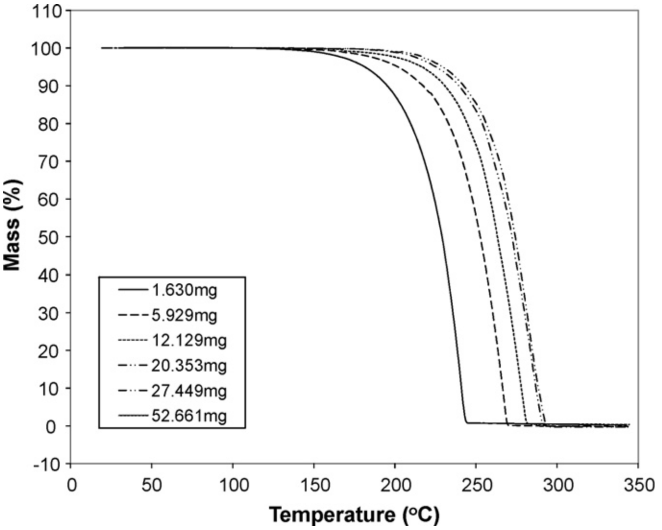

Fig. 4. Effect of sample mass on the mass loss profile (TGA signal) during the decomposition of pure ammonium nitrate in air with a flow rate of 100 ml min^{-1} in an alumina crucible. The heating rate was 10 K min^{-1}.

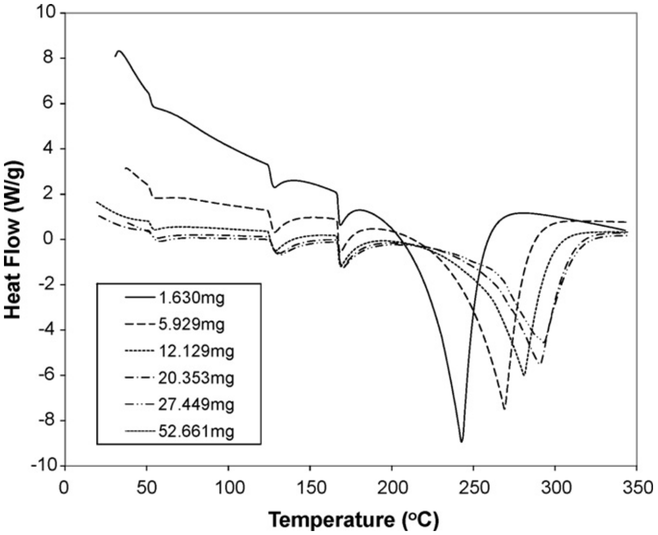

Fig. 5. Effect of sample mass on the heat flow profile (DSC signal) during the decomposition of pure ammonium nitrate in air with a flow rate of 100 ml min^{-1} in an alumina crucible. The heating rate was 10 K min^{-1}.

The effect of mass on the observed rate of decomposition of ammonium nitrate has not been reported often in the literature. Although the reaction mechanism and the kinetics of ammonium nitrate decomposition have been studied by many investigators, it was only reported by Koga and Tanaka [26,27] that the activation energy of ammonium nitrate decomposition decreases slightly with increasing sample mass in the range of 5–15 mg using TGA. These authors speculated that ammonium nitrate starts to decompose after melting and the decomposition occurs from the top layer of the sample and moves through to the bottom until decomposition is complete. The large effect of the sample mass shown in Figs. 4 and 5 indicates the necessity of finding the kinetics that is independent of sample mass used in the measurements. Therefore detailed experiments were conducted to study the effect of sample mass on the kinetic parameters of ammonium nitrate decomposition with an attempt to find the mass-independent kinetic parameters. This was achieved in the present research by investigating the effect of various experimental conditions such as reaction atmosphere, gas flow rate, type of crucible and heating rates on the kinetics of ammonium nitrate decomposition.

To perform the kinetic analysis, ammonium nitrate was decomposed at four different heating rates. Fig. 6 shows that, with increasing the heating rate, all the thermal peaks (two crystallographic transformation peaks, one melting peak and one decomposition peak) are shifted to higher temperatures. One would have expected that increasing the heating rate should not shift the first three peaks, as these peaks are governed by thermodynam-

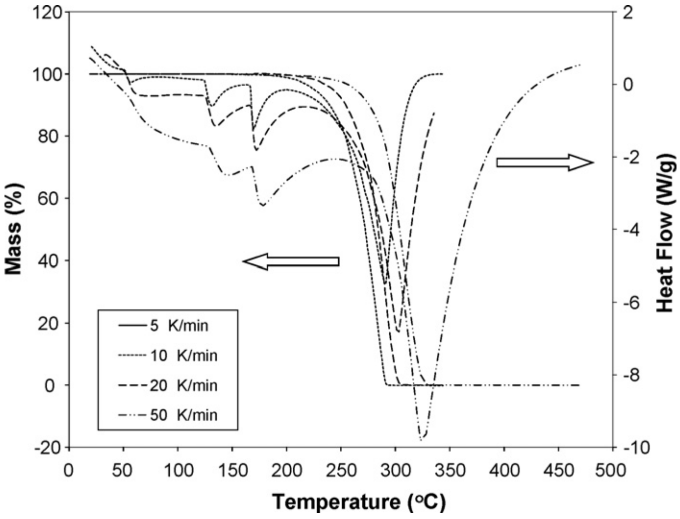

Fig. 6. Effect of heating rate on the decomposition of ~20 mg ammonium nitrate in air with a flow rate of 100 ml min^{-1} in alumina crucibles.

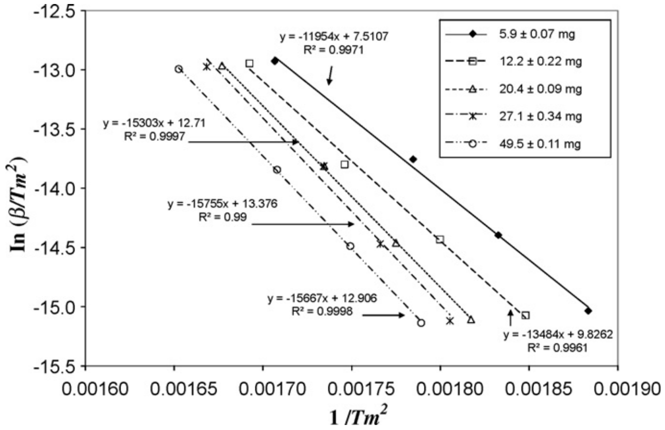

Fig. 7. $\ln(\beta/T_m^2)$ vs $(1/T_m)$ plots for the decomposition of ammonium nitrate at different sample masses.

ics. These shifts can be explained by the fact that a high heating rate will cause a greater thermal lag in the DSC–TGA instrument. The decomposition peak is expected to be shifted as it is kinetically controlled.

Fig. 7 shows such plots for 5 different sample masses of pure ammonium nitrate decomposition. The correlations shown in Fig. 7 suggest that the data are best fitted with Eq. (4) to obtain the kinetic parameters of ammonium nitrate decomposition.

However, variations in the activation energy with sample mass under different experimental conditions are shown in Fig. 8. The apparent activation energy increases from 102.5 to 136.2 kJ mol^{-1} when the sample mass increases from 5 to 50 mg. This trend is opposite to that reported by Koga and Tanaka [27]. It was initially thought that this difference would have been due to the reaction atmosphere (gas type and flow rate) or the crucible type. However, Fig. 8 also shows that the reaction atmospheres (air or nitrogen) and gas flow rate do not affect the kinetics of the decomposition of pure ammonium nitrate. Yet, it is shown in Fig. 8 that the values of activation energy obtained using the platinum crucible are lower than those obtained using the alumina crucible. It is worthy mentioning that a set of heating rates of 5, 10, 20, and 50 K min^{-1} was used with the alumina crucible, while a set of heating rates of 0.5, 1, 2.5 and 10 K min^{-1} was used with platinum crucible.

Fig. 9 shows that the mass loss and the heat flow of pure ammonium nitrate and a mixture of ammonium nitrate and alumina are very similar, indicating that different crucible type (platinum or alumina) has no significant effect on ammonium nitrate decomposition. Moreover, the activation energy values calculated using a set of heating rates of 0.5, 1, 2.5, and 10 K min^{-1} for the decomposition of ∼15 mg pure ammonium nitrate using the platinum crucible with and without added alumina powder are 93.7 and 94.1 kJ mol^{-1}, respectively. Therefore, the difference in the activation energy values obtained with the two types of crucibles is also insignificant.

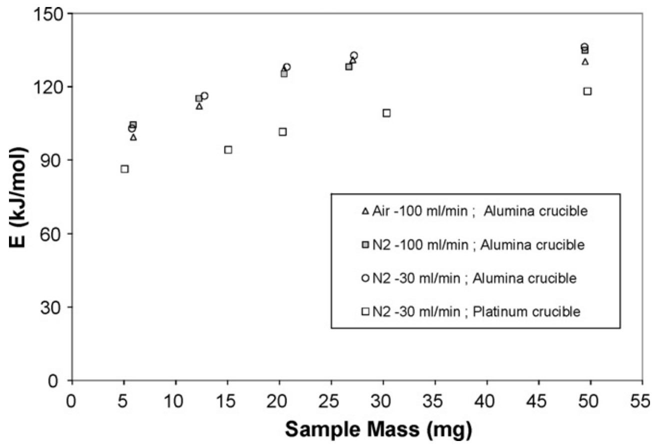

Fig. 8. Effect of reaction atmosphere, gas flow rate and type of crucible on the activation energy of ammonium nitrate decomposition.

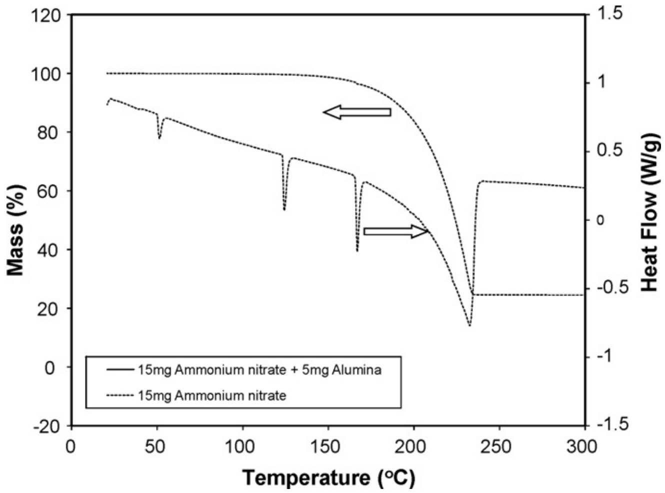

Fig. 9. Effect of added alumina on the decomposition of ammonium nitrate in nitrogen with a flow rate of 30 ml min^{-1} in the platinum crucible. The heating rate was 1 K min^{-1}.

Theoretically, the kinetics of the reaction, which is not controlled by any heat and/or mass transfer effects, should be independent of the heating rates used [31]. However, Fig. 10 clearly shows that the heating rate had a significant effect on the kinetics of ammonium nitrate decomposition for the higher masses of samples used. On the other hand, for the lower sample masses, the activation energies are relatively constant as expected. This observation suggests that both heat and mass transfer influence on the reaction process as studied in the DSC–TGA.

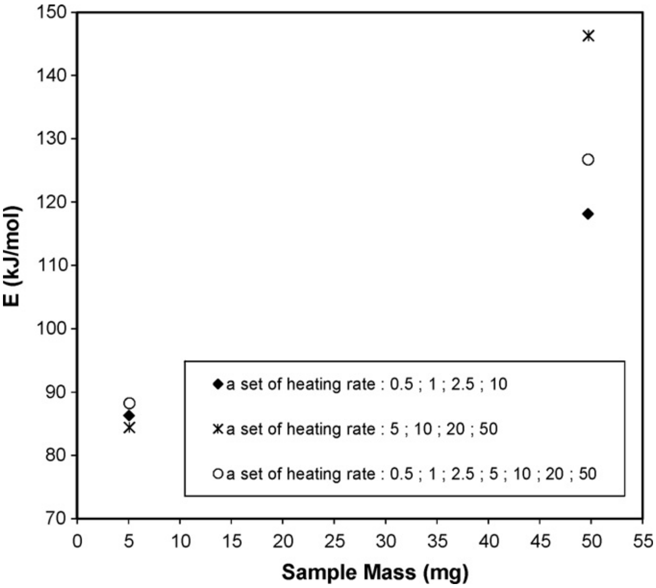

Fig. 10. Effect of heating rates on the activation energy of ammonium nitrate decomposition.

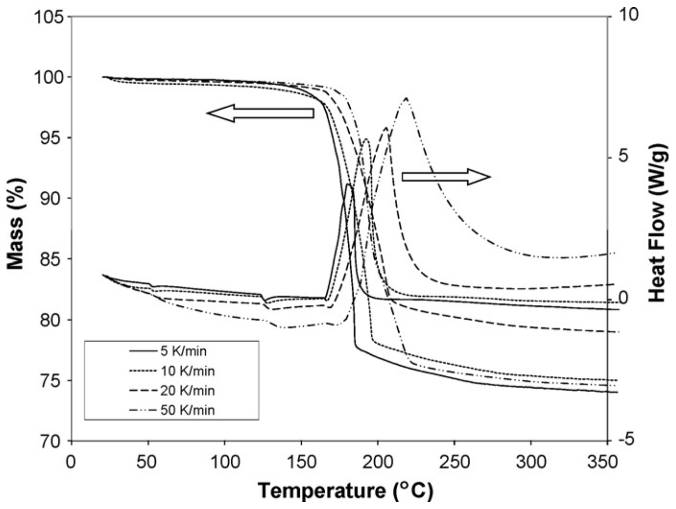

Fig. 11. DSC–TGA signals of ammonium nitrate decomposition in the presence of pyrite. The air flow rate was 100 ml min^{-1} and an alumina crucible was used.

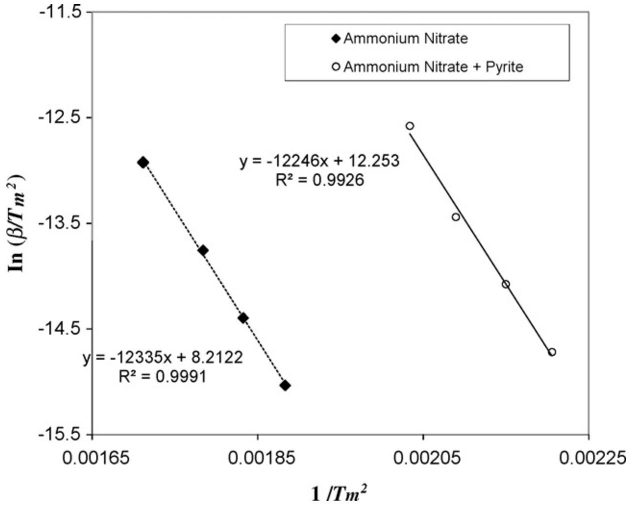

Fig. 12. $\ln(\beta/T_m^2)$ against $(1/T_m)$ plots for ammonium nitrate decomposition with and without the presence of pyrite.

Since the sample has a finite heat capacity, there is always a difference between temperature recorded by the thermocouple in the TGA, which is not in direct contact of the sample, and the actual temperature of the sample. For the higher sample masses, this thermal lag becomes more significant and cannot be neglected as the transport (heat and mass) processes also play a role in the reaction. The lower masses of samples in the TGA experiments should then provide more realistic kinetic data. Therefore 5 mg of ammonium nitrate, incurring the least transport effect in the present experimentation, was used in this study to determine the kinetics of ammonium nitrate decomposition that will be used to calculate the critical temperatures.

Table 2
The kinetic parameters determined from the DSC data.

Sample	E (kJ mol^{-1})	A (s^{-1})
Pure ammonium nitrate	102.6	4.55×10^7
Ammonium nitrate + pyrite	101.8	2.57×10^9

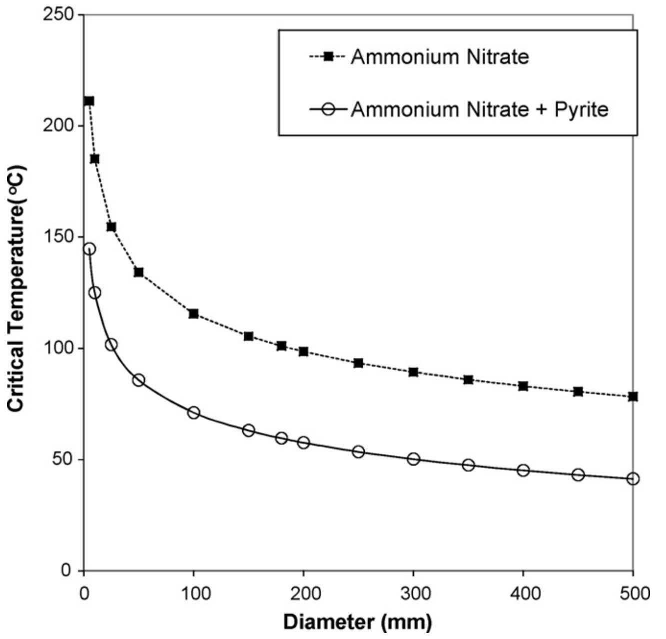

Fig. 13. The critical temperature as a function of blast hole diameter for ammonium nitrate decomposition with and without pyrite.

4.2. *The critical temperatures of ammonium nitrate decomposition with and without pyrite*

Based on the results of our preliminary investigations, the DSC–TGA tests of ammonium nitrate decomposition in the presence of pyrite were conducted using an alumina crucible and approximately 5 mg of ammonium nitrate. The DSC–TGA signals and the plots of $\ln(\beta/T_m^2)$ against $(1/T_m)$, according to Eq. (4), for ammonium nitrate decomposition in the presence of pyrite are presented in Figs. 11 and 12, respectively. The activation energy and pre-exponential factor for ammonium nitrate decomposition with and without pyrite are listed in Table 2. In order to calculate the critical temperature, other parameters required were obtained from the literature [10] and listed in Table 3.

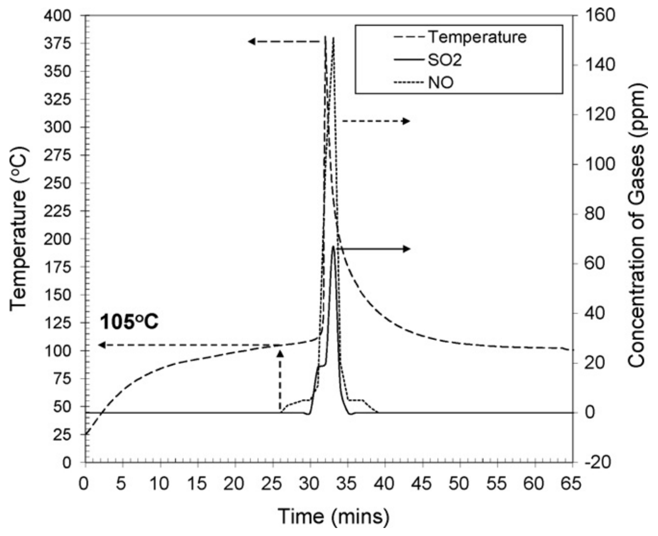

Fig. 14. The temperature and gas profiles of the mixture of 5 g ammonium nitrate and 15 g pyrite heated up to 105 °C in the isothermal gas-sealed reactor with argon as a carrier gas.

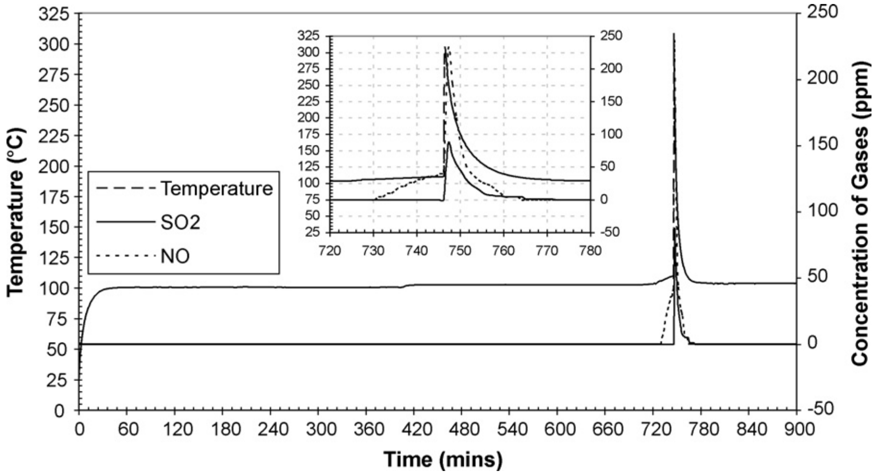

Fig. 15. The temperature and gas profiles of the mixture of 5 g ammonium nitrate and 15 g pyrite heated up to ∼100 °C and then to ∼103 °C in the isothermal gas-sealed reactor with argon as a carrier gas.

The critical temperatures were calculated for different blast hole diameters and the results are given in Fig. 13. It can be seen from Fig. 13 that the critical temperature decreases with an increase in the blast hole diameter. More importantly, Fig. 13 also demonstrates that the presence of pyrite significantly reduces the critical temperature of ammonium nitrate. For the diameter of a typical blast hole of 200 mm, the critical temperature is drastically decreased from 98.6 to 57.7 °C.

4.3. Validation of the predicted critical temperature of ammonium nitrate decomposition in the presence of pyrite

While the verification of the predicted critical temperature could not be made using real blast holes in this study, experiments were conducted to validate the result in the gas-sealed isothermal reactor with a diameter of 21 mm. In this verification experiments, 5 g ammonium nitrate was mixed with 15 g pyrite (the same ratio as in the DSC–TGA experiments). The mixture was placed in the reactor and argon was flowed to create an inert atmosphere. The mixture was then heated to 105 °C, while the temperature and the concentration of gases were monitored. The set temperature of 105 °C was selected based on the prediction of critical temperature calculated (Fig. 13) for the reactor diameter of 21 mm for which the critical temperature was predicted to be 105.9 °C.

Fig. 14 shows the results of this verification experiment using the gas-sealed isothermal reactor. It is very interesting to see that, although the onset temperature of the thermal runaway is around 110 °C, it is evident that at 105 °C, NO gas was emitted indicating that the ammonium nitrate decomposition in the presence of the pyrite has started.

Additional experiments were also conducted at lower temperatures, 90, 95 and 100 °C, respectively. It was found that the mixture did not react when they were held at those temperatures for up to 24 h. A further experiment was then conducted by heating the ammonium nitrate–pyrite mixture to and held at 100 °C for about 400 min. No reaction was observed. The temperature was then increased again, carefully, to ∼103 °C and at this temperature, the mixture incurred thermal runaway after 350 min, as shown in Fig. 15. A close inspection of the temperature and gas emission profiles (Fig. 15) revealed that NO gas was formed and emitted at around 105.5 °C. The above evidences strongly support that the prediction of critical temperature of ammonium nitrate in the presence of pyrite in the blast holes situation is reliable.

Table 3
Thermophysical parameters required for the calculation of the critical temperatures.

Parameters	Ammonium nitrate	Ammonium nitrate and pyrite
Density, ρ (gcm^{-3})	1.725[a]	2.77
Thermal conductivity, λ (W m^{-1} K^{-1})	0.142[a]	0.142[a]
Heat of reaction, Q (J m^{-3})	2.52×10^9[b]	1.74×10^9[b]

[a] Obtained from [10].
[b] Obtained from present DSC data.

It is interesting to note that both NO and SO$_2$ were detected from the isothermal reactor when ammonium nitrate is mixed with the pyrite, while it is known that endothermic decomposition of ammonium nitrate does not emit SO$_2$ [12–14,16,17]. It is clear that both NO and SO$_2$ are produced from the oxidation of pyrite by ammonium nitrate as previously discussed by the present authors [32].

The results of this study have significant implications in the rock blasting practice using ANFO in mining operations, especially in reactive mining grounds, as pyrite minerals present in some of the reactive ground have been shown to significantly reduce the thermal stability of ammonium nitrate.

5. Conclusions

Ammonium nitrate decomposition, with and without the presence of pyrite, has been studied and the activation energy and the pre-exponential factor of ammonium nitrate decomposition were determined to be 102.6 kJ mol^{-1} and 4.55×10^7 s^{-1} without the presence of pyrite and 101.8 kJ mol^{-1} and 2.57×10^9 s^{-1} with the presence of pyrite. The critical temperatures for ammonium nitrate decomposition, with and without the presence of pyrite, were calculated using the kinetic parameters thus determined and were shown to decrease with increasing the diameter of blast holes charged with the explosives. The presence of pyrite reduces the temperature and accelerates the rate of decomposition of ammonium nitrate. It has been further shown that pyrite can significantly decrease the critical temperature of ammonium nitrate decomposition, potentially causing undesired premature detonation of the explosives in the rock blasting practice using ANFO in mining operations, especially in reactive mining grounds containing pyrite minerals. For a typical blast hole diameter of 200 mm, the presence of pyritic reactive shale is shown to drastically decrease the critical temperature from 98.6 to 57.7 °C. A concept of using the critical temperature as indication of the thermal stability of the explosives to evaluate the risk of spontaneous explosion has been proposed and verified in the isothermal reactor experiments.

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