



Thermal hazard assessment of AN and AN-based explosives

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Abstract

Ammonium nitrate (AN) is an essential ingredient in most fertilizers. It is also widely used in the commercial explosives industry. In this latter application, it is mostly mixed with fuel oil to form the most popular commercial explosive: ANFO. In both the fertilizer and the explosive industry, aqueous AN solutions (ANS) of various concentrations are processed. These solutions also form the basis of ammonium nitrate emulsion explosives (also called ammonium nitrate emulsions or ANE), which are produced either in bulk or in packaged form.

For all these AN-based products, quantities of the order of 20,000 kg are being manufactured, transported, stored, and processed at elevated temperatures and/or elevated pressures. Correspondingly, major accidents involving overheating of large quantities of these products have happened in several of these operations. In comparison, convenient laboratory quantities to investigate thermal decomposition properties are generally less than 1 kg. As a result, in order to provide information applicable to real-life situations, any laboratory study must use techniques that minimize heat losses from the samples to their environment.

In the present study, two laboratory-scale calorimeters providing an adiabatic environment were used: an accelerating rate calorimeter (ARC) and an adiabatic Dewar calorimeter (ADC). Experiments were performed on pure AN, ANFO, various ANS systems, and typical bulk and packaged ANE systems. The effects of sample mass, atmosphere, and formulation on the resulting onset temperatures were studied. A comparison of the results from the two techniques is provided and a proposed method to extrapolate these results to large-scale inventories is examined.

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1. Introduction

In the first half of the last century, several major accidents involving ammonium nitrate (AN) occurred, principally as a result of poor knowledge of its thermal decomposition

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properties (for example: Oppau, Germany, 1921 [1]; Texas City, USA [2] and Brest, France [3], 1947). Since then, AN has been used in a large variety of fertilizer and explosive processes and, even if major modifications to these processes have reduced the occurrence of such accidents, the major explosion that recently occurred in Toulouse, France (September 2001) constitutes a severe reminder that much still remains to be learned about the hazards of AN. In fact, several more recent major accidents, often involving fatalities, have been associated with AN itself, ANFO, AN solution (ANS), and ammonium nitrate emulsion (ANE) systems (see [4–10] for examples). A review of these events reveals that thermal hazards should be the greatest concern with these energetic materials (EM).

Correspondingly, numerous experimental techniques have been developed to assess the thermal hazards of energetic materials. Differential scanning calorimetry (DSC), thermogravimetry (TG), and simultaneous differential thermal analysis (SDT) are the most common laboratory techniques. While these techniques are very useful for other purposes, it should be recognized that, due to the small associated sample size (1–2 mg), they cannot provide meaningful indications of safe operating temperatures for large-scale manufacturing processes.

When attempting to quantify the hazards associated with the manufacture and use of AN and AN-based explosives, a key parameter is the temperature at which these EMs begin to self-heat through runaway exothermic decomposition: the “onset” temperature (T_o). Self-heating occurs, for a particular material, when the rate of heat generation is greater than the rate of heat loss to the environment. For a given experimental or practical geometry, heat losses are greater for small samples, so T_o normally decreases with increasing sample size. As a consequence, any laboratory studies that aim to provide results that are applicable to large-scale situations must be designed so as to minimize heat losses to the environment.

Two laboratory-scale calorimeters that minimize heat losses by providing an adiabatic environment are the accelerating rate calorimeter (ARC) and the adiabatic Dewar calorimeter (ADC). In the present work, both techniques have been applied to study the onset of runaway reactions in AN, typical AN-based oxidizers, ANFO, ANS, and ANE systems. Both types of experiments were performed under “open” and “closed” configurations. For closed experiments, the system is sealed, allowing pressure to build up whereas for open experiments, the system is vented. It was anticipated that the closed and open experiments would provide information appropriate to confined pumping situations and vented storage vessels, respectively. Also the effects of sample mass and surrounding inert or oxidizing atmosphere were investigated in many cases.

A comparison of the T_o values obtained using the two techniques is presented. The applicability of the results to bulk quantities is also discussed.

2. Experimental

2.1. Materials

Ammonium nitrate (Sigma, ACS Grade, 100.1% assay), sodium perchlorate (SP, Sigma, ACS Grade, 99.6%) and sodium nitrate (SN, Fisher, ACS Grade, 99.9%) were used to

make up the dry oxidizers and oxidizer solutions. Other AN samples, containing mass levels of 0.1–4% of different clay additives were obtained from various manufacturers and tested as received. ANFO was prepared by mixing explosive grade AN prills with 5.7% by mass of No. 2 Diesel Fuel Oil. The ANEs were supplied by explosives manufacturers and tested as received. Both unsensitized bulk emulsion (UBE) and detonator sensitive emulsion explosives (DSEE) were investigated.

2.2. Accelerating rate calorimeter (ARC)

ARC minimizes heat losses by matching the temperature of the calorimeter walls to that of the sample: if the sample begins to self-heat, the temperature of the heaters in the walls is increased accordingly. Advantages of the ARC technique are that adiabatic conditions are achieved with rather small samples (1–3 g) and that the experiments can be carried out in a laboratory environment with minimal risks to people or equipment.

The experiments were carried out using one of the ARCs available at the Canadian Explosives Research Laboratory (CERL). This ARC is a commercial automated adiabatic calorimeter distributed by Arthur D. Little Inc. and is used for the purpose of assessing the thermal hazard potential of EMs [11]. Adiabatic conditions are maintained in the ARC provided that the rate of temperature increase does not exceed about $10\text{ }^{\circ}\text{C min}^{-1}$. Experiments were carried out using standard CERL procedures already described in earlier publications [12–14].

Since stainless steel is the most common material of construction in AN and AN-based explosives manufacturing facilities, a spherical sample vessel, made of 316 stainless steel, was used for each run. Each vessel was pre-treated by rinsing several times in distilled water, several times in acetone, followed by heating in an oven at $110\text{ }^{\circ}\text{C}$ for at least 2 h.

Two configurations were used for each sample—“closed” and “open”. For the closed experiments, the ARC manifold was closed in order to maintain any pressure resulting from vaporization or decomposition of the sample. For the open experiments, the sample vessel was still connected to the ARC manifold, but the latter was left open to the atmosphere, through a 0.8 mm internal diameter stainless steel line. No pressure could then build up in the ARC vessel and any gases generated during the decomposition of the sample were vented to the atmosphere. With the exception of a few experiments on ANFO and detonator sensitive emulsion explosives where argon was used, all experiments were run in an air atmosphere.

The history of sample temperature is obtained by a thermocouple mounted outside of the sample vessel, in direct contact with the stainless steel wall just under the sample. For all ramped experiments, the sample was heated quickly to $100\text{ }^{\circ}\text{C}$, equilibrated at this temperature and subsequently subjected to the standard ARC procedure of “heat–wait–search”. In this study, the temperature of the system was raised by $5\text{ }^{\circ}\text{C}$ and the system was maintained adiabatic during the “wait” period (30 min for dissipation of thermal transients) and the “search” period (20 min looking for an exotherm). An exotherm was defined as a self-heating rate (R) greater than a preselected threshold value of $0.02\text{ }^{\circ}\text{C min}^{-1}$. The temperature at this rate is a measure of the ARC onset temperature for decomposition. Since exotherms are not detected during the “heat” or “wait” modes, the “true” value of T_0 is obtained by extrapolating to $R = 0$. Whenever an exotherm is detected during the search mode,

the heat–wait–search procedure is automatically interrupted, and the calorimeter tracks the time, temperature and rate (calculated), and pressure. Data collection was programmed to stop if the pressure exceeded a set value (usually 6.89 MPa or 1000 psia), or R exceeded a certain value (usually $5\text{ }^{\circ}\text{C min}^{-1}$).

In some cases, isothermal experiments were also performed in order to find out if a sample maintained at a fixed temperature, usually lower than the measured T_0 value, could be pushed to runaway. For these experiments, the sample was heated quickly to the chosen fixed isothermal temperature and maintained adiabatic at this temperature until an exotherm was detected (same threshold value of $R > 0.02\text{ }^{\circ}\text{C min}^{-1}$). From this point on, the isothermal procedure was automatically interrupted, and the calorimeter was again allowed to track time, temperature, rate, and pressure.

2.3. Adiabatic Dewar calorimeter (ADC)

Good discussions of the ADC technique and how it compares to other thermal hazard assessment methods can be found in [15,16]. Typically, the sample is loaded into an insulated Dewar flask. The latter is then placed in an oven. The temperature of the sample is increased, either slowly by heat conduction from the oven, or by means of internal heaters. One advantage of the ADC technique is that it uses large samples (100 g and greater), so the relative heat losses to the sample container are small compared to ARC. A serious practical disadvantage, however, lies in the fact that runaway reactions on this scale can damage or destroy the apparatus, particularly when EMs are being studied. Because of this, ADC experiments involving EMs cannot be carried out in a laboratory environment, for safety reasons.

The ADC used in the present work was constructed in-house, at CERL. The Dewar flask and fittings were purchased from Avecia Ltd. of Blackley, England. Avecia was formerly part of the ICI Fine Chemicals Manufacturing organization, where the ADC technique was developed in the 1980s [16].

The detailed set-up chosen for the installation at CERL was designed so as to make the system as simple as possible, to facilitate reconstruction in the event of a severe uncontrolled reaction. Some years ago, such an ADC facility was destroyed at ICI Explosives Group Technical Centre in Ardeer, Scotland, when testing only 100 g of a packaged emulsion explosive [17]. As a result, the internal heaters and agitator commonly used in ADC experiments [15] were not employed here. Heating of the sample was achieved by slow conduction from the oven. The heating rate was controlled so as to produce “quasi-adiabatic” conditions. In addition, sample sizes of 100 g were chosen, substantially smaller than the 300–800 g samples used in the chemical industry.

A schematic of the experimental set-up is shown in Fig. 1. A 0.99 L stainless steel vacuum Dewar flask is located in a Thelco oven capable of operating up to $250\text{ }^{\circ}\text{C}$. The flask is fitted with the following: internal thermocouple, pressure transducer, proportional pressure relief valve and a remote vent valve. The flask was placed in the oven, which was housed in a blast containment chamber.

The operation of the experiment is controlled from a PC located in a separate instrument room. A data acquisition card (DAC) provides a terminal block for connections to sensors and control relays. Physically, the DAC also contains all the hardware necessary for measuring, digitizing, multiplexing and communicating with the PC. The hardware is

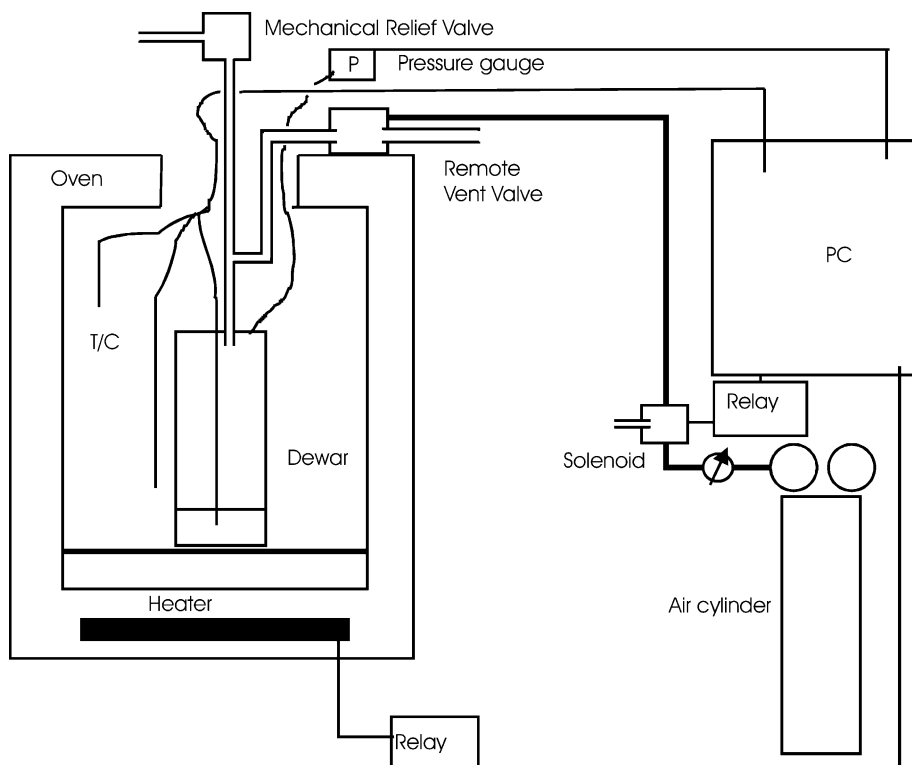


Fig. 1. Schematic diagram of the ADC.

configurable through an icon-based programming language (Workbench PC). This allows the PC to perform the following tasks: (i) monitoring of the two oven thermocouples and the sample thermocouple, as well as the sample pressure; (ii) control of the heating rate of the oven by actuating a relay; (iii) control of the operation of a remote vent valve, using a relay to provide gas pressure to the actuator of the valve.

The temperature of the oven can be held isothermal or can be ramped. To achieve ramping, an average oven temperature is obtained from two thermocouples, one above the Dewar and one close to the neck of the flask, and used to control ramping of the oven. The ramp rate is controlled from a user panel. Altering of the amplitude and frequency of a triangular pulse that is generated by the program sets the rate.

For the work described here, a simple experimental procedure was developed during the course of the study:

- (i) The oven was heated rapidly to a specified initial temperature. It was then held isothermally until the sample temperature was close to that of the oven. Because of the excellent insulating properties of the Dewar, wait periods of 24 h were typical. The initial temperature was generally chosen to be 25 °C below the anticipated T_0 value, which was generally assumed to be 15 °C below that measured in the ARC.

- (ii) Once the sample temperature had stabilized close to the oven temperature, the latter was ramped at $2.16\text{ }^{\circ}\text{C h}^{-1}$. The ramp was continued until either significant self-heating was detected or the sample pressure exceeded a pre-set value, at which point the system was tripped out. Significant self-heating was assumed once the sample temperature exceeded the oven temperature. The pressure trip was set to be above the pressure seen in the early stages of self-heating in the corresponding ARC experiment (typically 1–2 MPa).
- (iii) When a trip condition was met, the oven was shut down immediately, cooling rapidly. The oven temperature normally cools down from 200 to $100\text{ }^{\circ}\text{C}$ in approximately 40 min, with a maximum sample cooling rate close to $50\text{ }^{\circ}\text{C h}^{-1}$. In addition, a trip condition caused the automatic actuating of the remote vent valve, releasing the pressure in the Dewar vessel. This pressure release provided further cooling of the sample through adiabatic expansion. The amount of cooling depends on the pressure being relieved. Rapid cooling of up to $50\text{ }^{\circ}\text{C}$ was observed for systems with pressures close to 1.0 MPa (150 psia).

2.4. Evaluation of Phi-factors, ϕ

Both the ARC and the ADC methods described above use ‘quasi-adiabatic’ conditions to minimize the heat losses from the sample to its surroundings. However, the sensitivity of the method is also controlled by the heat losses from the sample to the sample vessel. This is usually characterized by a parameter ‘ ϕ ’ defined as:

$$\phi = \frac{m_s c_s + m_c c_c}{m_s c_s} \quad (1)$$

where m_s and m_c are the masses of the sample and the vessel, respectively. Similarly, c_s and c_c are the heat capacities per unit mass of the sample and vessel, respectively. The importance of ϕ is discussed in detail in [11]. Clearly, it can be minimized either by limiting the mass of the vessel, or by increasing the mass of the sample.

The values of ϕ for both calorimeters have been determined by modeling the heat transfer properties of the systems [18]. For the ARC, an effective ϕ was estimated by comparing the results of full simulations with those obtained by setting the heat capacity of stainless steel and temperature gradients at the surface of the sample vessel to zero. Equating ϕ to the ratio of initial self-heating rates gave $\phi = 2.9$ for a 3 g sample of AN in the sample vessel. Repeating the simulation with 1 g of AN, with and without heat losses to the ARC sample vessel gave $\phi = 6.4$. If ϕ scaled simply with mass, a value of $\phi = 8.7$ would be expected. This result demonstrates that the effective ϕ for ARC experiments can be a complex function of the masses of both the sample and the vessel. Moreover, the heat capacity of the sample is also expected to vary with temperature so that the dynamic value of ϕ may vary significantly during a typical experiment.

Using a similar modeling approach for the ADC with 100 g of AN, ϕ is predicted to lie in the range 1.2–1.5 [19]. In this case, an attempt was also made to measure ϕ using the following procedure: Different masses of water, preheated to $80\text{ }^{\circ}\text{C}$, were added to the Dewar flask, which was then inserted rapidly into the oven and the lid fitted as per a normal experiment. Both the Dewar and the oven were initially at ambient temperature. The

sample thermocouple was then used to measure the initial temperature of the water in the Dewar.

Values of ϕ were calculated using:

$$\phi = \frac{80.0 - T_a}{T_{s,\text{initial}} - T_a} \quad (2)$$

where T_a and $T_{s,\text{initial}}$ refer to the ambient and initial sample temperature, respectively. The results demonstrate that ϕ decreases with increasing sample size, as expected. Values of $\phi = 1.16$ and 1.35 were obtained with 500 and 100 g of water, respectively.

Correcting for the difference in heat capacities of water and AN gave $\phi = 1.6$ for 100 g of AN. Although none of the above procedures give an unequivocal value of ϕ under dynamic temperature-ramped conditions, it is clear that ϕ is at most equal to 1.6 and probably considerably less. Setting $\phi = 1.6$ should give a worst-case scenario for extrapolation of the ADC data. This latter value is also observed to be much smaller than the above values for the ARC.

2.5. Evaluation of onset temperatures (T_o)

The procedure adopted in the present work to determine the T_o values is essentially the same for both calorimeters. For the ARC, they were obtained by extrapolating the initial slope of the exotherms to $R = 0$, using the rate versus T plots. The extrapolation was performed by eye and the resulting uncertainties were evaluated from the onset temperatures obtained using the maximum and minimum slopes of straight lines representative of the data. For the ADC, the same procedure was adopted except that the data, from the rate versus T plots, were extrapolated to the oven heating rate ($2.16^\circ\text{C h}^{-1}$).

3. Results

The results of all ARC experiments are presented in [Tables 1 and 2](#). The results of the ADC experiments are compared with those of the corresponding ARC experiments in [Table 3](#).

3.1. AN

3.1.1. ARC experiments

Three ARC runs with dry AN (1 and 3 g) gave very similar results, with T_o values close to 200°C . There was no change in T_o with mass for the two closed experiments. The open experiment had a slightly lower T_o value, but a much slower, multi-stage runaway: self-heating was detected at 200°C , but dropped below the ARC threshold between 210 and 220°C , before finally running away.

The behavior of AN (1 g) with various levels of additives was also investigated and corresponding temperature versus time records are shown in [Fig. 2](#). Due to the proprietary nature of these additives, they have only been identified by a number (1–7). It is seen that

Table 1
Summary of ARC data for AN, ANFO, dry oxidizers, and ANS

Sample	Mass (g)	System	Atmosphere		T_o (°C)	Remarks
			P_1 (MPa)	Gas		
AN (dry)	1.001	Closed	0.1	Air	200 ± 5	Runaway
AN (dry)	3.001	Closed	0.1	Air	199 ± 7	Runaway
AN (dry)	3.021	Open	0.1	Air	197 ± 5 217 ± 5	1 weak exotherm; $R_{max} = 0.04$ °C min ⁻¹ Runaway
ANFO	3.033	Closed	0.1	Air	194 ± 7	Runaway, sample vessel exploded
ANFO	1.002	Closed	0.1	Air	170 ± 7 238 ± 5	8 weak exotherms; $R_{max} = 0.04$ °C min ⁻¹ Runaway
ANFO	1.005	Closed	1.0	Air	166 ± 10 245 ± 10	1 early exotherm; $R_{max} = 0.04$ °C min ⁻¹ Runaway
ANFO	1.009	Closed	0.1	Argon	190 ± 10 236 ± 12	1 early exotherm; $R_{max} = 0.02$ °C min ⁻¹ Runaway
ANFO	1.088	Open	0.1	Air	185 ± 10 224 ± 5	2 early exotherms; $R_{max} = 0.03$ °C min ⁻¹ Runaway
Diesel fuel	0.174	Closed	0.1	Air	–	No exotherm up to 350 °C
Diesel fuel	0.171	Closed	1.0	Air	210 ± 7 285 ± 5	1 early exotherm; $R_{max} = 2$ °C min ⁻¹ Final exotherm; $R_{max} = 0.3$ °C min ⁻¹
Diesel fuel	0.171	Closed	0.1	Argon	240 ± 8 322 ± 6	1 early exotherm; $R_{max} = 0.02$ °C min ⁻¹ Final exotherm; $R_{max} = 0.04$ °C min ⁻¹
ANS 1% H ₂ O	3.029	Open	0.1	Air	220 ± 6	Runaway
ANS 2.5% H ₂ O	3.184	Open	0.1	Air	194 ± 2 222 ± 5	1 early exotherm; $R_{max} = 0.25$ °C min ⁻¹ Runaway
ANS 5% H ₂ O	3.056	Open	0.1	Air	221 ± 4	Runaway
ANS 10% H ₂ O	3.006	Open	0.1	Air	215 ± 5	Runaway
ANS 20% H ₂ O	1.031	Open	0.1	Air	227 ± 4	Runaway
ANS 20% H ₂ O	2.998	Open	0.1	Air	223 ± 5	Runaway
ANS 30% H ₂ O	3.034	Open	0.1	Air	222 ± 4	Runaway
ANS 40% H ₂ O	3.059	Open	0.1	Air	221 ± 4	Runaway
ANS 10% H ₂ O	1.014	Closed	0.1	Air	223 ± 5	Runaway
ANS 10% H ₂ O	3.022	Closed	0.1	Air	222 ± 5	Runaway
ANS 20% H ₂ O	1.026	Closed	0.1	Air	237 ± 5	Runaway
ANS 20% H ₂ O	2.990	Closed	0.1	Air	242 ± 5	Runaway
AN/SN/SP (dry)	0.999	Closed	0.1	Air	197 ± 3	Runaway
AN/SN/SP (dry)	3.002	Closed	0.1	Air	193 ± 2	Runaway
AN/SN/SP (dry)	3.002	Open	0.1	Air	193 ± 2 222 ± 4	1 early exotherm; $R_{max} = 0.08$ °C min ⁻¹ Runaway
AN/SN/SP/H ₂ O (13% H ₂ O)	1.006	Closed	0.1	Air	233 ± 4	Runaway
AN/SN/SP/H ₂ O (13% H ₂ O)	3.091	Closed	0.1	Air	231 ± 5	Runaway
AN/SN/SP/H ₂ O (13% H ₂ O)	3.028	Open	0.1	Air	223 ± 8	Runaway

P_1 : initial pressure, T_o : onset temperature, R_{max} : maximum rate of self-heating.

Table 2
Summary of ARC data for ANE systems

Sample	Mass (g)	System	Atmosphere		T_o (°C)	Remarks
			P_i (MPa)	Gas		
UBE	1.221	Closed	0.1	Air	220 ± 5 237 ± 8	1 early exotherm; $R_{\max} = 0.12$ °C min ⁻¹ Runaway
UBE	3.168	Closed	0.1	Air	227 ± 5	Runaway, sample vessel exploded
UBE	3.065	Open	0.1	Air	210 ± 6	Runaway
DSEE 1	1.022	Closed	0.1	Air	223 ± 4 252 ± 8	1 early exotherm; $R_{\max} = 1.2$ °C min ⁻¹ Runaway
DSEE 1	1.007	Closed	0.1	Air	224 ± 2	Early exotherm not separated from main exotherm
DSEE 1	1.041	Closed	0.1	Argon	232 ± 3	Runaway
DSEE 1	2.994	Closed	0.1	Air	231 ± 6	Runaway
DSEE 1	3.031	Closed	0.1	Air	232 ± 6	Runaway
DSEE 1	3.002	Open	0.1	Air	201 ± 5	Runaway
DSEE 1	1.033	Open	0.1	Air	195 ± 11	Holes in sample vessel, only weak exotherm, no runaway
DSEE 2 (2001)	1.000	Closed	0.1	Air	219 ± 5	Runaway
DSEE 2 (2001)	1.002	Closed	1.38	Air	145 ± 6 210 ± 5	1 early exotherm; $R_{\max} = 0.08$ °C min ⁻¹ Runaway
DSEE 2 (2002)	1.024	Closed	1.38	Air	145 ± 6 230 ± 5	1 early exotherm; $R_{\max} = 0.05$ °C min ⁻¹ Runaway
DSEE 2 (2002)	3.018	Closed	1.38	Air	150 ± 6 215 ± 5	1 early exotherm; $R_{\max} = 0.07$ °C min ⁻¹ Runaway
DSEE 2 (2001)	1.020	Closed	1.38	Air		Isothermal experiment, $T_i = 150$ °C; $t_o = 35.3$ h
DSEE 2 (2002)	1.000	Closed	0.1	Air		Isothermal experiment, $T_i = 170$ °C; $t_o > 41.4$ h
DSEE 2 (2002)	1.020	Closed	1.38	Air		Isothermal experiment, $T_i = 160$ °C; $t_o > 53.2$ h
DSEE 2 (2002)	1.024	Closed	1.38	Argon		Isothermal experiment, $T_i = 170$ °C; $t_o > 39.8$ h
DSEE 2 (2002)	1.007	Closed	1.38	Air		Isothermal experiment, $T_i = 170$ °C; $t_o = 20.7$ h
DSEE 2 (2002)	1.019	Closed	3.45	Air		Isothermal experiment, $T_i = 170$ °C; $t_o = 9.9$ h
DSEE 2 (2002)	3.039	Closed	3.45	Air		Isothermal experiment, $T_i = 170$ °C; $t_o = 6.3$ h
DSEE 2 (2002)	1.038	Closed	6.89	Air		Isothermal experiment, $T_i = 170$ °C; $t_o = 4.6$ h

P_i : initial pressure, T_i : initial isothermal temperature, T_o : onset temperature, R_{\max} : maximum rate of self-heating, t_o : time to runaway defined arbitrarily as the time from the beginning of the isothermal run to the point where the self-heating rate attains 0.5 °C min⁻¹.

Table 3
Summary of results for ADC experiments and comparison with ARC results

Sample	System	ADC		ARC		Remark
		Mass (g)	T_o ($^{\circ}\text{C}$)	Mass (g)	T_o ($^{\circ}\text{C}$)	
AN (dry)	Closed	99.9	192 ± 5	3.001	200 ± 5	Runaway
AN (dry)	Open	100.9	187 ± 10 219 ± 5	3.021	197 ± 5 217 ± 5	Start of self-heating Runaway
ANFO	Closed	100.3	160 ± 3 223 ± 5	1.002	170 ± 7 238 ± 5	Start of self-heating Runaway, ADC destroyed
ANFO	Open	100.1	167 ± 4 180 ± 7	1.088	185 ± 10 224 ± 5	Start of self-heating Runaway
ANS (10% H ₂ O)	Closed	100.0	213 ± 5	3.022	222 ± 5	Runaway
ANS (20% H ₂ O)	Closed	100.0	217 ± 5	2.990	242 ± 5	Runaway
ANS (10% H ₂ O)	Open	100.3	205 ± 5	3.006	215 ± 5	Runaway
ANS (20% H ₂ O)	Open	100.1	207 ± 5	2.998	223 ± 5	Runaway
AN/SN/SP (dry)	Closed	100.0	180 ± 5	3.002	193 ± 2	Runaway
AN/SN/SP (dry)	Open	100.0	170 ± 5	3.002	193 ± 2 222 ± 4	Start of self-heating Runaway
AN/SN/SP/H ₂ O (13% H ₂ O)	Closed	100.0	210 ± 5	3.091	231 ± 5	Runaway
AN/SN/SP/H ₂ O (13% H ₂ O)	Open	100.0	203 ± 5	3.028	223 ± 8	Runaway
UBE	Closed	100.0	184 ± 5 218 ± 5	3.168	227 ± 5	Start of self-heating Runaway, ARC sample vessel exploded
UBE	Open	100.4	183 ± 5	3.065	210 ± 6	Runaway, ADC damaged

while additives 1 and 2 decreased the value of T_o by up to 15°C , additive 7 increased the latter by about 40°C . It is also observed that the other additives did not significantly change the T_o value for AN. These results show that the use of additives 1 or 2 in a full scale AN manufacturing facility could compromise safety and that the ARC constitutes an excellent screening tool for this purpose.

3.1.2. ADC experiments

Experiments with pure AN present a challenge with the ADC apparatus, as exothermic decomposition begins close to the melting point. The initial oven temperature (175°C) was chosen so that the AN would just melt during the isothermal period. Unfortunately, heat transfer is very slow when the oven temperature is only slightly above the sample temperature. Phase changes during the initial heating period could be clearly seen (Fig. 3). The temperatures of the phase changes agree well with the known literature values of 32 , 85 , and 125°C [20]. The T_o value for AN in the closed Dewar was $192 \pm 5^{\circ}\text{C}$ compared to 199 ± 7 for the ARC. In the open system T_o was somewhat lower at $187 \pm 10^{\circ}\text{C}$ compared to $197 \pm 5^{\circ}\text{C}$ in the ARC.

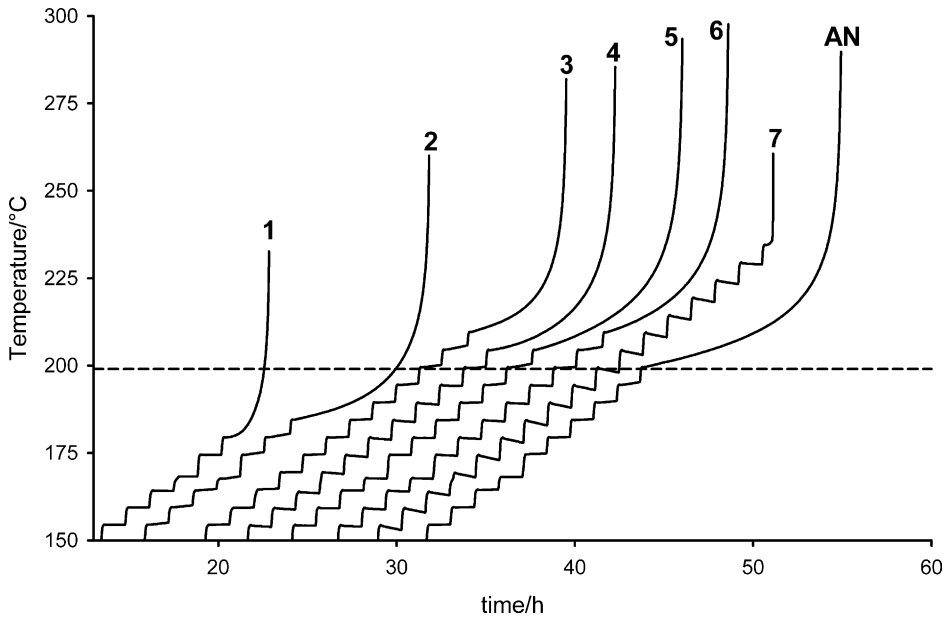


Fig. 2. Comparison of ARC heat-wait-search data for AN and AN + various clay additives. Curves have been shifted in time for clarity.

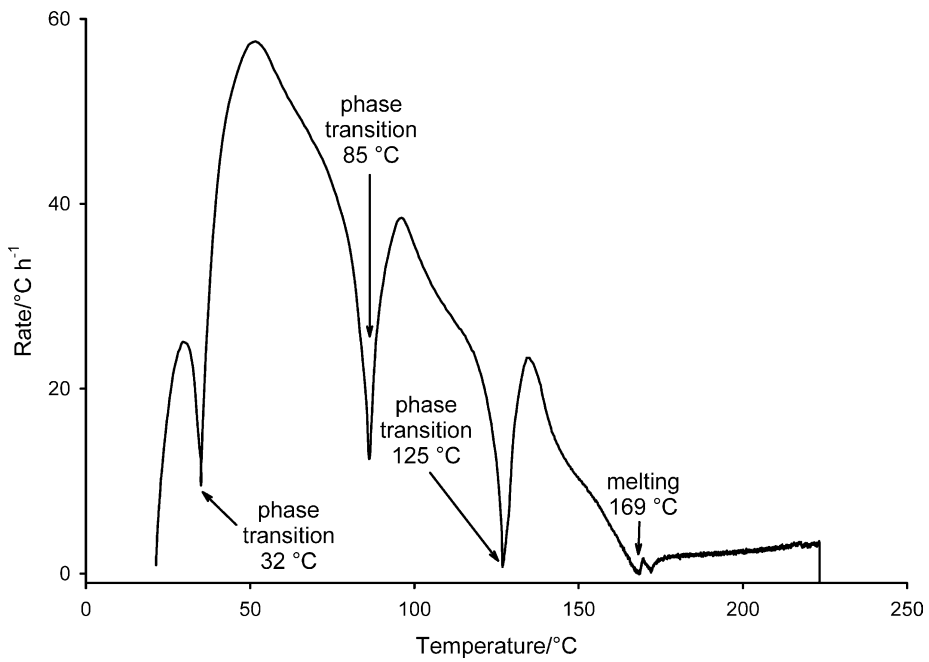


Fig. 3. Rate vs. temperature plot for ADC experiment with 100 g of pure AN.

3.2. ANFO

3.2.1. ARC experiments

From the present experiments, the thermal decomposition of ANFO appears to be even more complex than that of AN, owing to the presence of the fuel. In order to minimize ϕ , the first experiment with ANFO was carried out with a 3 g sample. This sample started to self-heat at 200 °C and quickly ran away causing rupture of the ARC sample vessel. Subsequent experiments used 1 g samples and there were no further uncontrolled reactions with the resulting increase in ϕ .

With 1 g of ANFO, there was a complex series of exotherms beginning at temperatures as low as 170 °C. These early exotherms were weak and did not lead to runaway. The final exotherm began at about 235 °C. It can be seen from Fig. 4 that the sample began to generate pressure at a temperature as low as 125 °C, providing further evidence for a weak reaction at even this low temperature. Both the open and closed system runs produced similar series of mild exotherms with very little difference in the T_o value. To ascertain if the early weak exotherms were due to the oxidation of the oil phase, ARC runs of ANFO in argon and at 1 MPa of air were carried out. In argon a very weak exotherm at about 200 °C was followed by a final exotherm starting at 236 °C. At 1 MPa of air a weak exotherm began at 166 °C followed by a final exotherm at about 245 °C.

Several ARC runs were carried out with 0.1 g fuel oil alone (mass equivalent to 2 g of ANFO). In ambient air no exothermic activity was detected up to 350 °C. At 1 MPa of air a weak exotherm was detected at 210 °C followed by a final exotherm at 285 °C. However, no runaway reaction was observed in this case. In ambient argon, again no significant

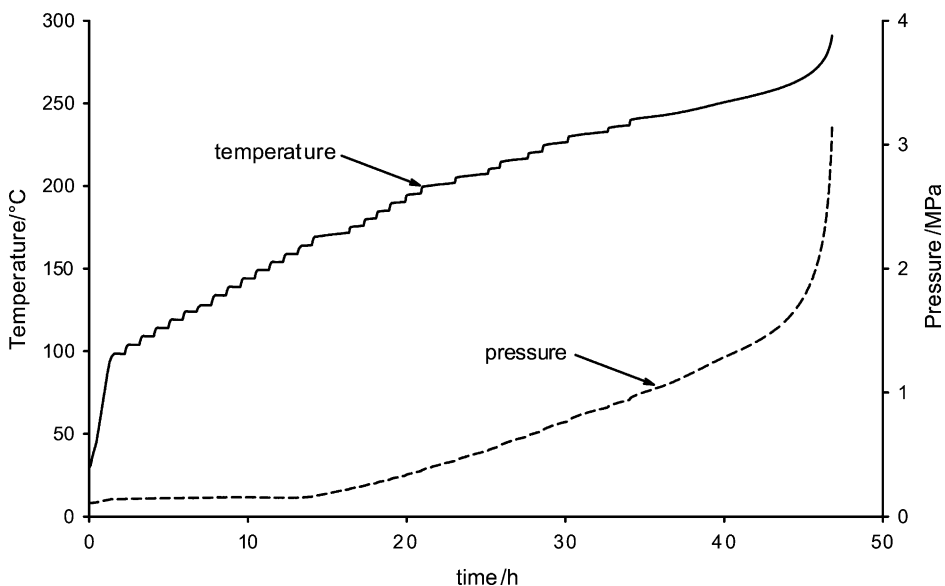


Fig. 4. Typical temperature and pressure history for ANFO (ARC, closed system).

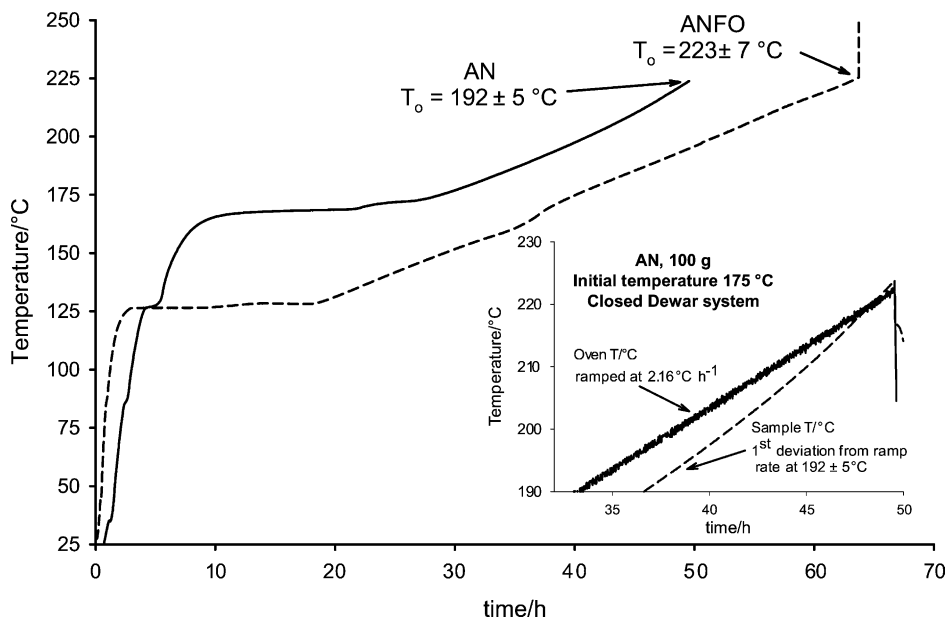


Fig. 5. Temperature history for AN and ANFO in ADC closed experiments.

exothermic activity was observed up to 350 °C. From these results, it would appear that the early weak exotherms noted with ANFO may be due to an interaction of the fuel oil with AN, or the dissociation products of AN, and not strictly oxidation of the fuel oil.

3.2.2. ADC experiments

With 100 g of ANFO in the ADC using the open configuration, signs of self-heating were first detected at about 167 °C with a final runaway starting around 180 °C. In the closed configuration weak exotherms were detected at temperatures as low as 160 °C and a very fast, violent exothermic reaction starting at about 223 °C completely destroyed the Dewar flask and the oven.

A Dewar run of 5.7 g of fuel oil (mass equivalent to 100 g ANFO) in the open system showed no sign of self-heating up to 250 °C.

When ANFO is heated while open to the atmosphere the onset of self-heating begins at a lower temperature and proceeds at a slower rate. In a closed system the onset of self-heating and the rate of reaction are both much higher. A comparison of the behavior of AN and ANFO in the ADC is shown in Fig. 5.

3.3. ANS

3.3.1. ARC experiments

ARC experiments were carried out on ANS systems with water content from 0 to 40 mass%. Additional experiments on a typical AN/SN/SP oxidizer system, in both dry and solution form, were also performed. Fig. 6 shows the measured T_o values as a function

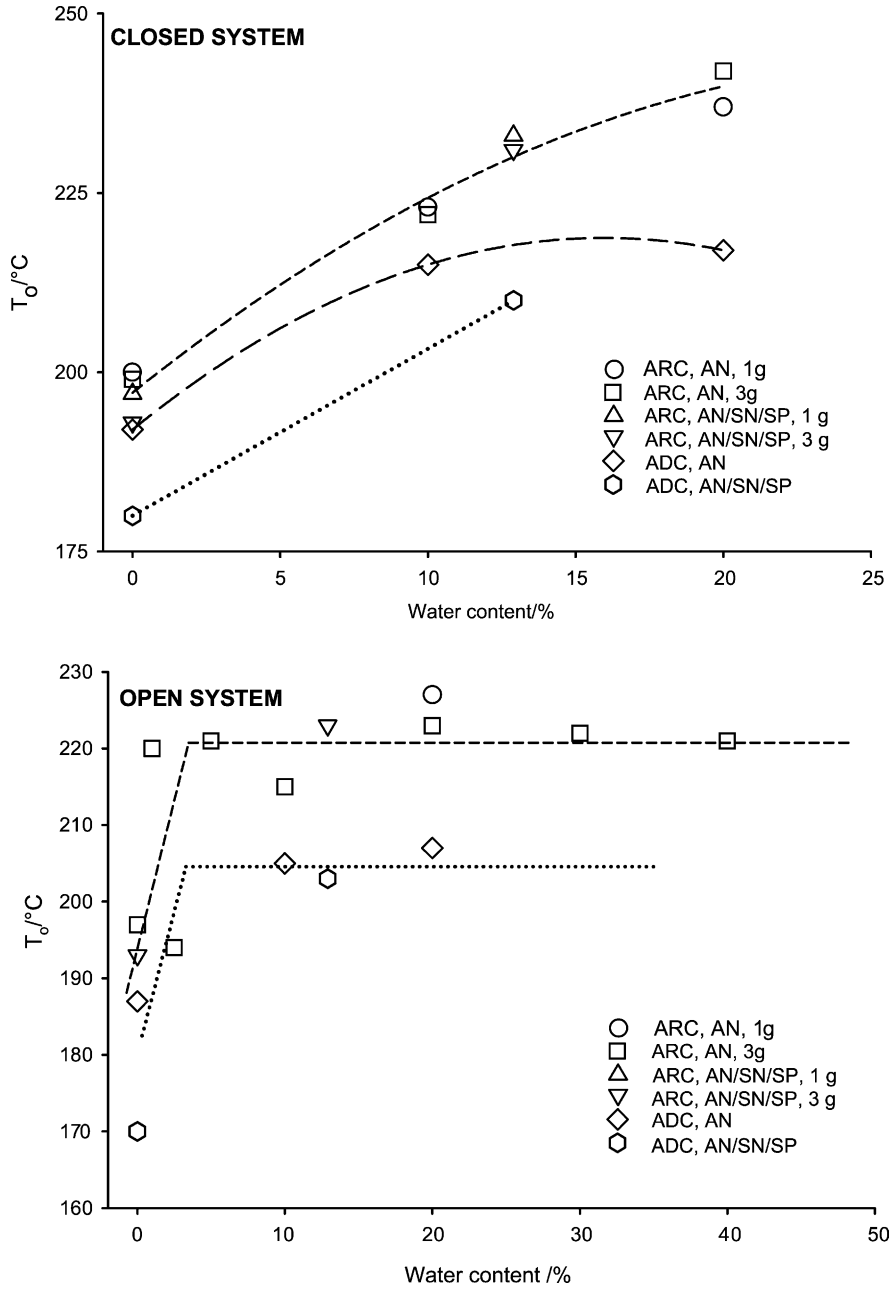


Fig. 6. Onset temperatures of various ANS systems in closed (top) and open (bottom) systems.

of water content for open and closed experiments, respectively. The open and closed systems display very different behavior. In open experiments, T_o increases quickly with water level and then remains roughly constant with water content up to 40 mass%. In contrast, T_o increases steadily with water content in the closed experiments. Again, the data display no systematic dependence on the sample mass. The behavior of the AN/SN/SP/H₂O system is also observed to be very similar to the ANS systems.

3.3.2. ADC experiments

In general, closed ADC experiments on ANS systems proceeded very smoothly. Some structure could be seen in the rate versus T plot between 70 and 100 °C, presumably owing to the dissolution of AN.

A typical example of the rate versus T plot for a 90 mass% ANS is shown in Fig. 7. It can be seen that, once the temperature ramp had begun, the sample heating rate increased smoothly to the oven heating rate and remained there for several hours before signs of self-heating were first observed at 215 ± 5 °C.

On the other hand, the analysis of ADC experiments in open configuration is complicated for systems, such as ANS, where large vaporization effects are expected. Because of the slow heat transfer to the sample, there is a thermal lag of a few degrees between the oven temperature and the sample temperature during the ramp period.

The sample also takes several hours to reach the nominal heating rate of the oven. Significant vaporization during the temperature ramp can cause the sample to take longer than

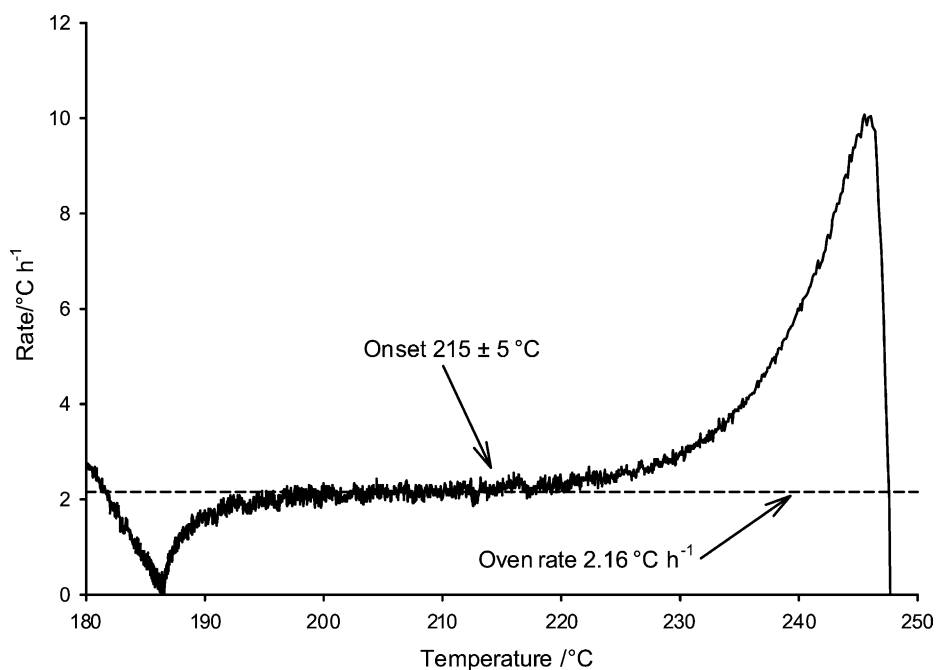


Fig. 7. Rate vs. temperature plot for a 90 mass% AN solution (ADC, closed system).

expected to reach the oven heating rate. This thermal lag is greatest in systems where vaporization is important. One result of an increased thermal lag is that the heat transfer into the sample is greater than expected. While the sample is undergoing significant vaporization, the heat of vaporization balances the additional heat flux. However, if the vaporization slows down, e.g. when most of the water has vaporized from an oxidizer solution, the heating rate of the sample can slightly exceed that of the oven until the equilibrium thermal lag is re-established. Careful analysis is required to avoid mistaking this effect for early self-heating.

This is illustrated in Fig. 8 for the case of an AN/SN/SP solution. Both the sample heating rate (left axis) and the oven/sample temperature lag (right axis) are plotted as a function of the sample temperature. The self-heating rate climbs steadily to about $2.5\text{ }^{\circ}\text{C h}^{-1}$ and remains quite stable until an acceleration is seen above $200\text{ }^{\circ}\text{C}$. It was initially thought that the early self-heating, between 170 and $190\text{ }^{\circ}\text{C}$ was a real effect. However, the thermal lag was high during the initial stages of the final ramp, reaching a maximum of $12\text{ }^{\circ}\text{C}$, compared to more typical values of $6\text{--}8\text{ }^{\circ}\text{C}$ for dry samples. In addition, the self-heating rate did not stabilize until 15 h after the ramp was started, compared to the expected 8 h . Moreover, no unusual structure in the rate versus temperature curve was observed in the corresponding ARC experiment. The conclusion from these observations is that the early self-heating starting around $175\text{ }^{\circ}\text{C}$ was an artifact due to the slowing down of the vaporization. Not enough evaporation was allowed before the final ramp was begun. As a result, the T_0 value was taken to be where the final acceleration of the self-heating rate occurred: $203 \pm 5\text{ }^{\circ}\text{C}$.

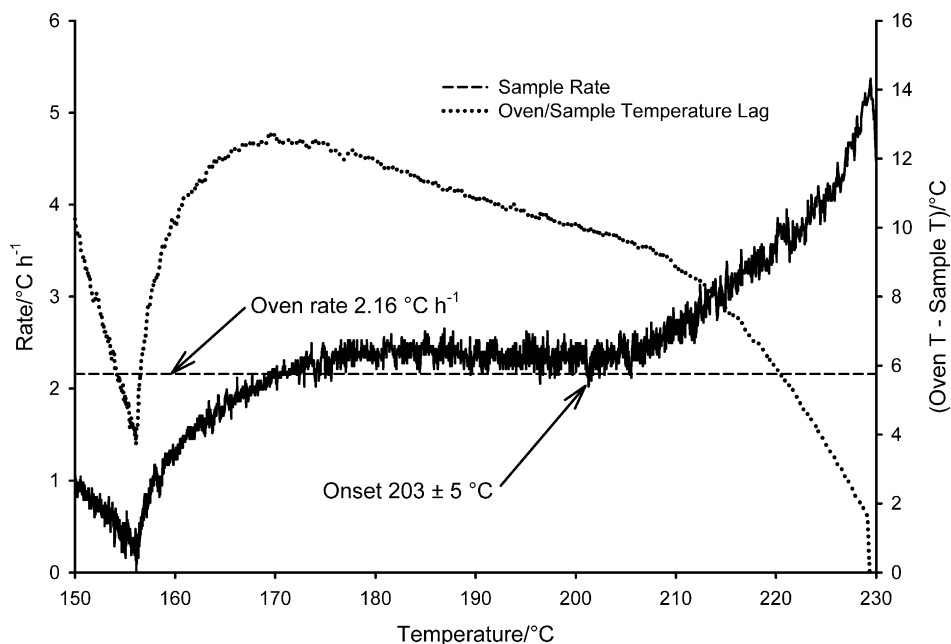


Fig. 8. Rate of temperature rise and oven/sample temperature lag vs. temperature for a AN/SN/SP solution (ADC, open system).

From Fig. 6, it is also seen that the trends noted in Section 3.3.1 were confirmed in the ADC experiments. However, due to the greater sensitivity and the lower ϕ of the ADC, the T_o values measured using this latter technique are about 15 °C lower than measured by ARC.

3.4. ANE

3.4.1. Unsensitized bulk emulsion (UBE)

The ARC experiments with a UBE system gave interesting results. The open experiment gave a T_o of 210 °C, substantially below the values measured for the closed experiments (220 and 227 °C). The closed experiments both displayed complex exotherms, with an “early”, slow self-heating that was more or less separated from the main exotherm (see Fig. 9). Unusually, the closed experiment with the larger sample (3 g) displayed a T_o value 7 °C higher than that of the smaller sample (1 g). The rapid final runaway in the 3 g experiment caused the ARC sample vessel to explode.

In the closed ADC experiment, the sample reached the initial ramp temperature (160 °C) with no sign of self-heating. After the start of the temperature ramp, the sample reached the oven ramp rate after approximately 10 h, and remained almost constant for several hours until distinct self-heating began at 184 ± 5 °C (Fig. 9). The self-heating continued until the sample reached close to 200 °C, then slowed down to below the oven heating rate. As the sample was heated further, self-heating began again at 218 °C, at which point the pressure

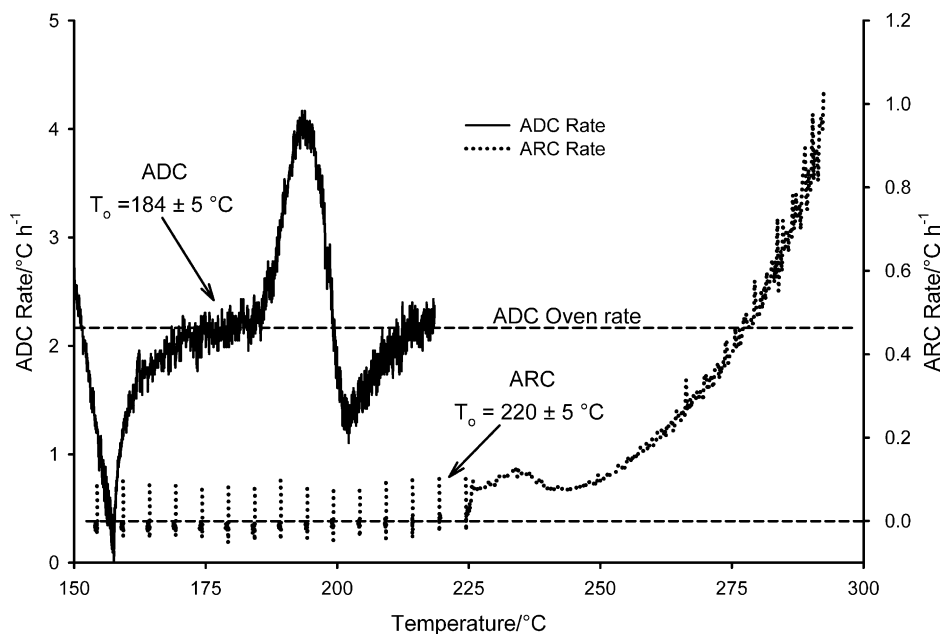


Fig. 9. Rate vs. temperature plots for unsensitized bulk emulsion (ADC and ARC, closed system).

trip was actuated. Similar behavior was observed in the corresponding ARC experiments: weak self-heating, followed by a drop in the self-heating rate and then a final runaway reaction.

In open ADC experiments, the results were complex and more difficult to interpret. Firstly, the sample took 65–70 h to get close to the oven temperature. A distinct break at 130 °C in the T versus t curve was seen, corresponding to emulsion breakdown. After this temperature, the heating rate was very slow, as material was boiled off. After careful analysis of the temperature lag versus T curve, the final exotherm appeared to begin at 183 ± 5 °C. The exotherm displays a complex structure, which could be caused by early reaction of the oil phase, as seen with the closed experiments.

It should be noted that, in one of these open experiments, the acceleration of the sample heating rate at the end of the experiment was too fast for the reaction to be quenched by oven cooling. The experiment ran away completely, with the sample temperature reaching close to 600 °C. The entire sample was consumed but, fortunately, there was no significant damage to the system.

3.4.2. Detonator sensitive emulsion explosives (DSEE)

Several ARC experiments were performed on two different DSEE systems having similar water content but containing different oil phases and chemical sensitizers. Again, due to the proprietary nature of the precise formulations, they will be referred to as DSEE 1 and DSEE 2. Also, due to the fact that considerable damage was caused by the previous ADC experiments with the UBE system, it was decided that only ARC experiments would be performed with the DSEE systems.

Several ARC experiments were carried out with DSEE 1. The observed behavior was complex. The two closed experiments with an air atmosphere and 1 g of sample demonstrated an early self-heating that was distinguishable from the main runaway exotherm (Fig. 10), similar to the experiments with bulk emulsion. No such precursor was observed with the 3 g samples in air, the open experiments, or with a 1 g sample in an inert argon atmosphere. The T_o value for the 1 g samples in air was 8 °C below that for the 3 g samples, but the T_o value of the 1 g sample in argon was the same as that of the 3 g samples.

Finally, an open experiment was carried out with a 1 g sample in a modified sample vessel. Instead of allowing gases to escape through the neck of the vessel and the 1.6 mm tubing of the ARC system, three 6.4 mm holes were drilled in the upper half of the vessel, to allow air to circulate more easily. This latter experiment gave a low T_o (206 °C), but no strong exotherm; the maximum self-heating rate was only 0.03 °C min^{-1} .

Additional ARC experiments were performed with DSEE 2. In this case, one set was carried out in 2001, with fresh product, while a second set took place in 2002, about 1 year later. In the earlier 2001 closed experiment at ambient air pressure, a single exotherm starting at 219 °C was observed. In a second experiment at elevated initial air pressure (1.38 MPa), a distinct mild exotherm was observed starting at about 145 °C while runaway was seen to take place at 210 °C (see Fig. 11, top). In order to find out if the heat generated by the first mild exotherm would be sufficient to push the system to runaway, an isothermal experiment was carried out. The system was quickly heated to 150 °C and held adiabatic at this temperature until an exotherm was detected. From that point on, the calorimeter tracked

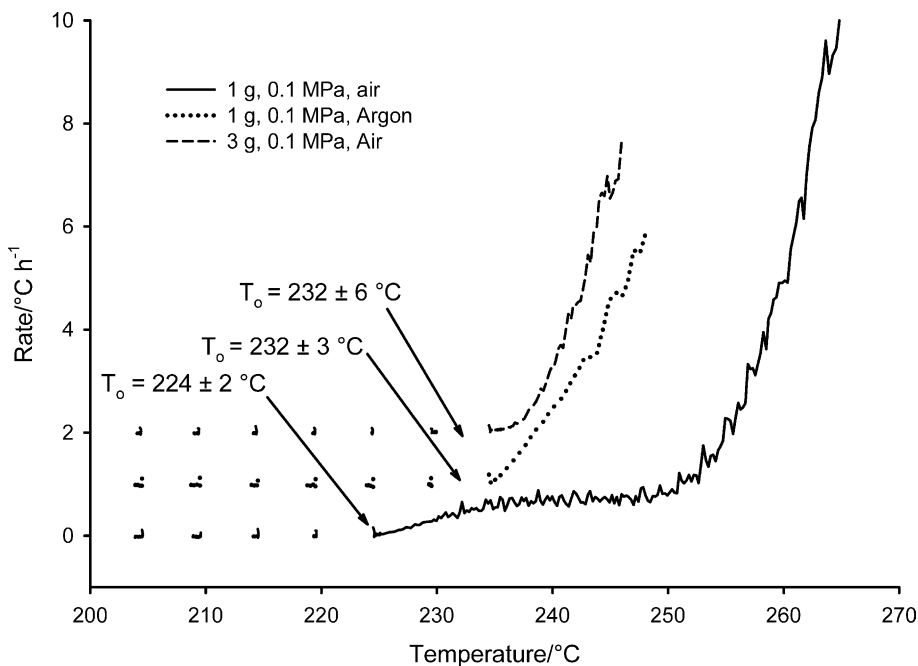


Fig. 10. Rate vs. temperature plots for various ARC runs with DSEE 1 (closed systems). Curves have been shifted in rate for clarity.

the sample temperature. It was found that the system could be pushed to runaway after 35 h (see Fig. 11, bottom).

In a repeat of these experiments in 2002, it was found that significant aging of the samples had occurred after 1 year during which they were stored in a heated and ventilated magazine. In the closed experiment with 1.38 MPa initial air pressure, the rates of self-heating for both the early and the final exotherms was observed to be significantly lower (see Fig. 11, top). Also, the onset of runaway was determined to occur at 230 °C, 20° higher than in the 2001 experiment. Moreover, in an isothermal experiment at 160 °C with the same initial air pressure (1.38 MPa), the system could not be pushed to runaway even after waiting for 53.2 h.

Following these observations, a series of isothermal experiments with varying initial atmosphere and sample mass was performed at 170 °C. The results are illustrated in Fig. 12. With an initial 1.38 MPa atmosphere of argon, no exothermic activity could be detected even after a 40 h residence time. With an initial air atmosphere, the observed behavior changed very significantly with increasing initial pressure: while no exotherm was detected with 0.1 MPa of air, the time to runaway was observed to become shorter and shorter from 21 h, at 1.38 MPa, to 10 h, at 3.45 MPa, and finally to 5 h, for a 6.89 MPa initial pressure. The effect of increasing sample mass was also investigated in identical experiments with 1 and 3 g samples for an initial air pressure of 3.45 MPa. In this case, the time to runaway was found to decrease by 30%, from 10 h, for the 1 g sample, to 6 h, for the 3 g sample.

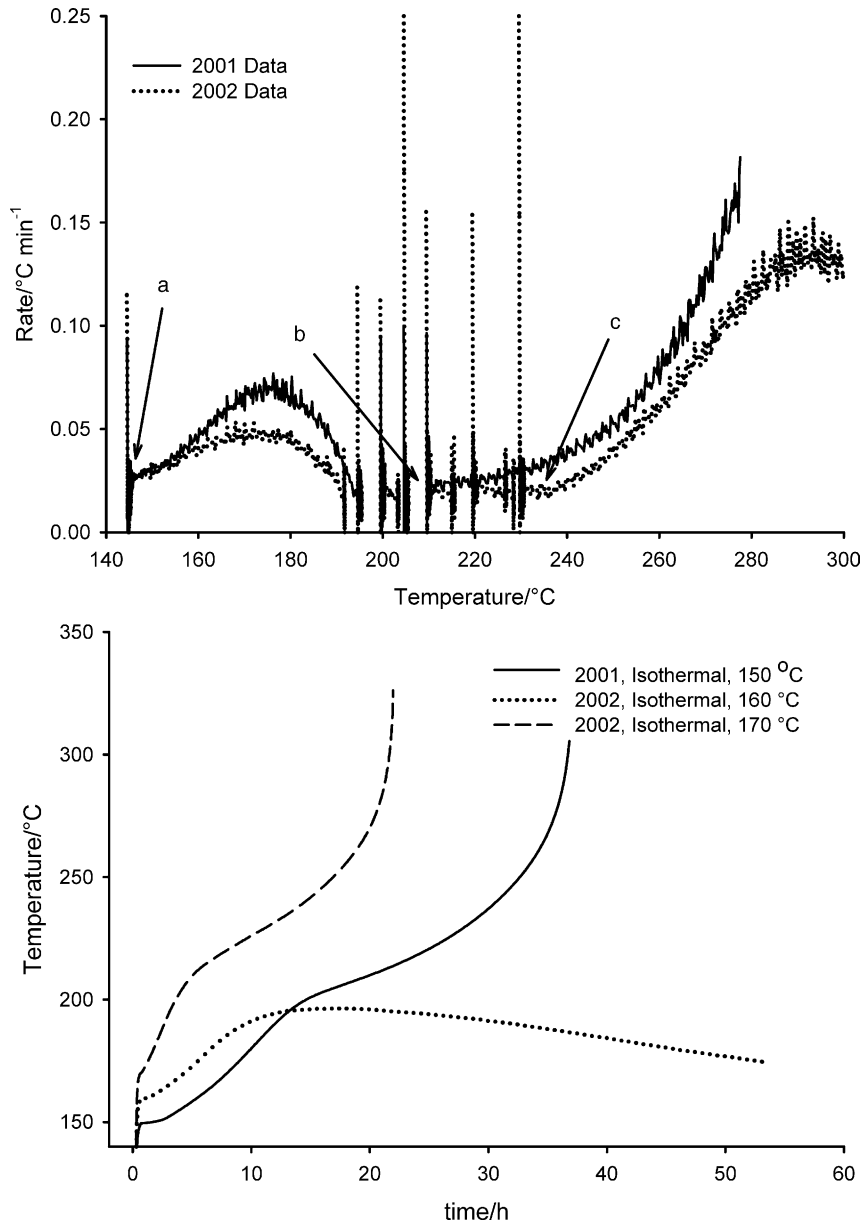


Fig. 11. Effect of aging on the thermal stability of DSEE 2 (ARC, closed system, initial pressure 1.38 MPa of air). Top, comparison of rate vs. temperature: (a) onset of first exotherm at 145 °C for both 2001 and 2002 experiments; (b) onset of runaway for 2001 experiment (210 °C); (c) onset of runaway for 2002 experiment (231 °C). Bottom, comparison of temperature vs. time for isothermal runs at various initial temperatures.

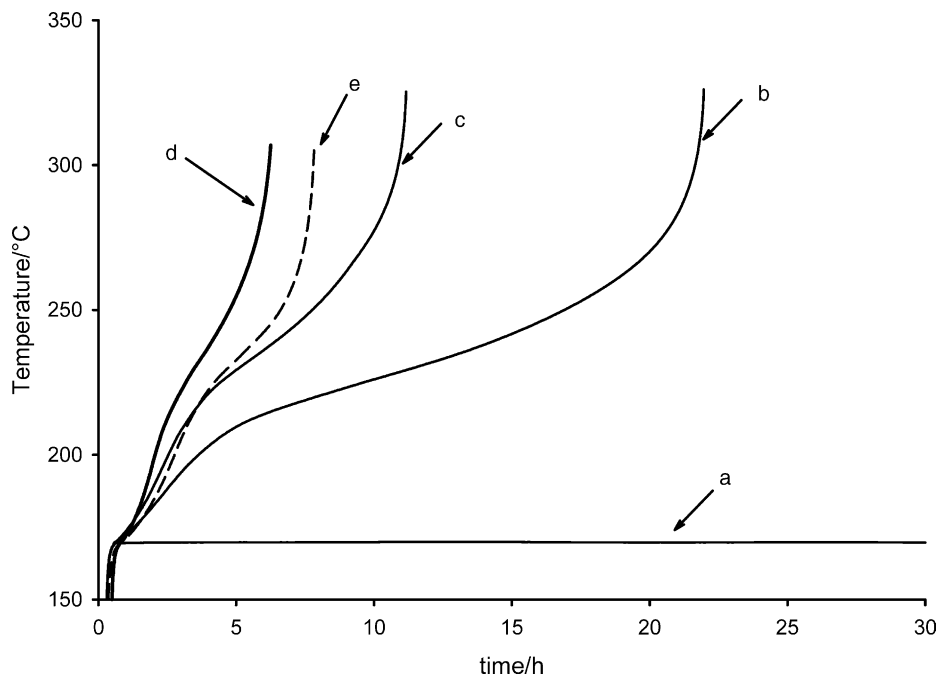


Fig. 12. Effect of atmosphere, initial air pressure, and initial sample mass on the onset of runaway in isothermal runs on DSEE 2 (ARC, closed system, initial temperature 170 °C); (a) 1 g, 1.38 MPa argon; (b) 1 g, 1.38 MPa air; (c) 1 g, 3.45 MPa air; (d) 1 g, 6.89 MPa air; (e) 3 g, 3.45 MPa air.

4. Discussion

4.1. AN and ANS

As would be expected from the lower estimated ϕ , the measured ADC T_0 values for AN are lower than those obtained by ARC. As seen from Table 3, the results obtained for an open system are also consistently lower than for a closed system, using both methods. This can be attributed to the fact that, in open systems, ammonia and water vapor can escape, leaving behind a more acidic sample. It is well known that the thermal decomposition of AN is acid-catalyzed. The effect of water is both physical and chemical: large amounts of water act as a heat sink, slowing reaction. It is also known that water in the gas phase suppresses the thermal decomposition of AN, therefore removing water vapor through venting will promote reaction.

From the evidence obtained in the present work (Fig. 2), it is obvious that even small quantities of contaminants can promote exothermic AN decomposition at lower temperatures. This is likely to represent a significant source of hazards, especially for the AN manufacturing industry where large quantities are being handled and where high temperature processing under limited flow conditions may produce long residence times.

It is clear from Fig. 6 that the T_o value of ANS in vented systems is essentially independent of water content above a few percent. At 220 °C, the vapor pressure of a 98 mass% ANS is equal to atmospheric pressure [21], so that more concentrated solutions will concentrate down to close to this level, but not further. It can be seen from Table 3 that the T_o values of 90 and 80 mass% AN solutions (ANS) are very close in open ADC experiments, providing further confirmation. The ADC and ARC T_o values for AN/SN/SP and ANS are very close in open systems, despite the different oxidizer mixtures. As a result AN and AN/SN/SP oxidizer solutions can be treated as the same from the point of view of maximum safe operating temperatures for vented systems.

For oxidizer solutions in closed systems, the key parameter appears to be the water content. The value of T_o increases steadily with water content and the ARC T_o value for the AN/SN/SP solution at 13 mass% water lies between those for the 80 and 90 mass% AN solutions. The ADC T_o value for the AN/SN/SP solution is slightly lower than those for the ANS, however, so a greater margin of safety would be required to prevent thermal runaway. The recommended margins of safety for these systems will be discussed in Section 4.3.

The dry oxidizers have the lowest T_o values of all the samples studied, including the emulsions. A conservative approach to prevention of thermal runaway would thus be to limit the temperature to below that of the least stable dry oxidizer, with an appropriate safety margin.

Detailed inspection of the rate versus temperature plots shows that, for many of the dry oxidizers, the runaway reactions are complex. In open systems, for example, there is clearly more than one stage to the decomposition. In many cases, Arrhenius plots from both the ARC and the ADC exotherms are obviously non-linear. It is not surprising that the kinetics of decomposition of these materials is complex, as the decomposition itself is complex, and involves a number of consecutive and simultaneous reactions and phase equilibria, as described in detail by Kolaczowski [22]. The initial step involves the endothermic dissociation of AN:



Subsequent reactions of ammonia and nitric acid are complex and ultimately generate heat through the formation of thermodynamically favored products such as nitrogen and water. Although the initial dissociation is endothermic, it is not separated from the subsequent reactions (which may be endothermic or exothermic) and the decomposition normally has to be looked at as a whole. One important consequence of the initial dissociation is that closed systems behave very differently from open systems. In open systems, vaporization of AN can occur easily and significant loss of the starting material can occur.

A few more interesting observations should also be pointed out. Firstly, although T_o values for vented systems are lower than for closed systems, the times to runaway are also longer in general. For the ARC, this time to runaway is arbitrarily defined as the time period between the onset of self-heating ($R > 0.02\text{ °C min}^{-1}$) and the highest detected sample temperature (usually corresponding to $R = 5\text{ °C min}^{-1}$). The longer times to runaway could be caused by greater evaporative heat losses during decomposition in the open experiments.

Secondly, the time to runaway generally decreases with increasing T_o . Fig. 13 shows a plot of $\ln(\text{time to runaway})$ versus $1/T$ for the ARC experiments for these systems. For each system (AN closed, AN/SN/SP open, etc.), the different points refer to different water

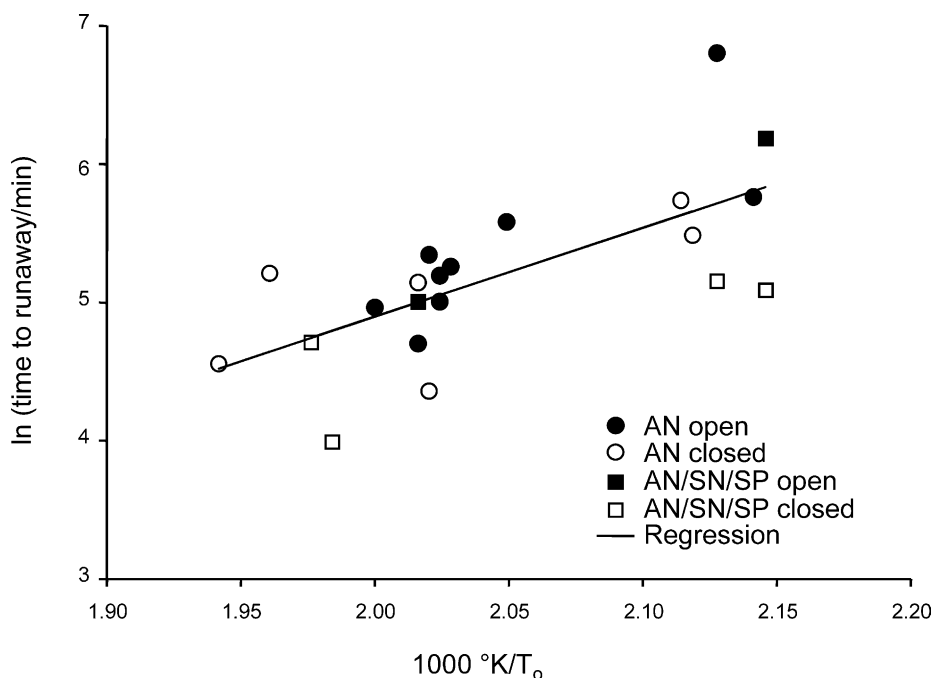


Fig. 13. Plot of $\ln(\text{time to runaway})$ vs. $1/T_0$ for ARC experiments with oxidizers.

levels. There is appreciable scatter in the plot, but a significant decrease in time to runaway with increasing T_0 is observed. The four systems studied behave similarly, although the times to runaway for the closed AN/SN/SP experiments do appear to be somewhat shorter than for the other systems. This general agreement implies that the overall kinetics has similar temperature dependence in each case.

4.2. ANFO and ANE

The thermal decomposition of ANFO and AN-based emulsions appears to be even more complex than that of the oxidizers, owing to the presence of the oil phase. In general, when air is present in sufficient quantity, early signs of self-heating can be detected at temperatures as low as 145–160 °C. Under temperature-ramped mode, this early exotherm appears to be fairly well decoupled from the final runaway exotherm. This is generally even more accentuated in ADC experiments, as the initial ratio of free air volume to sample volume is much higher in the latter, especially when compared with the ARC runs for which 3 g of sample material were loaded in the vessel.

From the present experiments on ANFO and diesel fuel oil, it appears that this first low temperature exotherm may be due to a reaction between the oil phase, ambient air, and AN (or early AN dissociation products). This reaction is not strictly oxidation of the oil phase since no such low temperature exotherm could be detected with the oil phase alone.

A body of evidence also suggests that this early exotherm may be due to a gas phase reaction between the volatile part of the oil phase, ambient air, and AN (or AN early dissociation products): firstly, significant aging of the DSEE 2 system is observed after 1 year. Long-term storage of the samples may promote migration of the volatile portion of the oil phase out of the system. After 1 year this may result in a lower concentration of fuel in the gas phase as the sample is heated in the ARC. This interpretation would be consistent with the observed 20 °C increase in onset temperature after 1 year. It is also consistent with the 20 °C increase in isothermal temperature required to push the system to runaway.

Secondly, the two DSEE systems studied in the present work differ mainly by the nature of the oil phase and it is seen that the first exotherm appears at much lower temperature for DSEE 2. More complete information about the respective oil phases would be required to find out if this may be explained by a higher volatility of the DSEE 2 oil phase.

Thirdly, in the closed experiments on the UBE system, the ADC value for T_o is seen to be as much as 40 °C lower than for the corresponding ARC experiments. This cannot be solely accounted for by the difference in ϕ . The higher initial free air volume in the Dewar, compared to the ARC sample vessel, may explain this unusual low T_o value. The fact that the oil phase is expected to float on top of the oxidizer phase after emulsion breakdown would then facilitate evolution of volatile fuel in the air free volume.

One important finding of the present work is that this early exotherm is sufficiently energetic to push the system to runaway. Both the initial amount of air present and the mass of the sample play a determining role in defining the necessary induction time for runaway to occur. As seen from the results of the closed ADC experiment on UBE, for which the value of T_o was about 40 °C lower than in the ARC, we may expect that relatively lower isothermal temperatures would push the system to runaway in the ADC.

4.3. Extrapolation to real-life quantities

In principle, an estimate of the T_o value applicable to storage or transportation vessels can be obtained by extrapolating the measured self-heating rate, corrected for ϕ , to the maximum cooling rate applicable for those vessels. For a 20 m³ vessel, a limiting safe self-heating rate of 0.0018 °C min⁻¹ should be representative and conservative, based on a review of several hazard assessment techniques [15].

In the case of the ADC apparatus, examination of the rate versus temperature plots demonstrates that departures from the oven heating rate of the order of 0.1 °C h⁻¹ (0.0017 °C min⁻¹) can be detected with the present experimental procedure. This value is well below the ARC threshold of 1.2 °C h⁻¹ (0.02 °C min⁻¹), confirming the much greater sensitivity of the ADC. This sensitivity is very close to the above limiting rate for a 20 m³ vessel so that very little extrapolation should be required.

Due to this much greater sensitivity of the ADC, exotherms are detected much earlier than in the ARC. Therefore, in order to compare extrapolations from both systems, only the very early stage of the ARC exotherm data should be used. Examples of such extrapolation are shown in Fig. 14 for AN and ANS systems. In these cases, value of 1.6 and 2.9 were used for the ϕ of the ADC and the ARC (3 g), respectively, as discussed in Section 2.4.

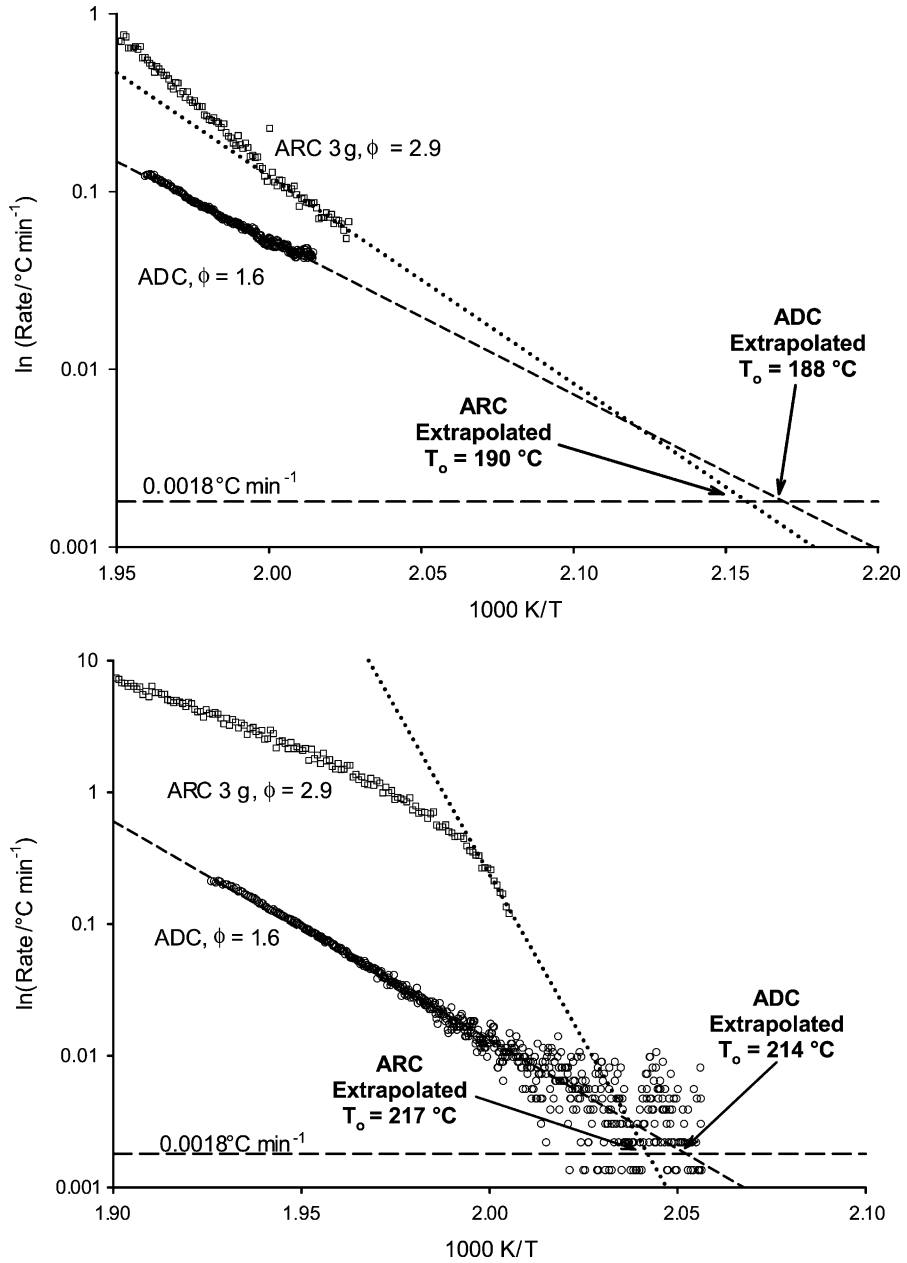


Fig. 14. Typical Arrhenius plots used in the extrapolation of ARC and ADC data for dry AN (open system, top) and an AN/water system (90/10, closed system, bottom).

Table 4

Summary of extrapolated ADC and ARC (3 g) onset temperatures for dry oxidizers and oxidizer solutions (20 m³ vessel)

Sample	System	ADC extrapolated T_o (°C)	ARC (3 g) extrapolated T_o (°C)
AN (dry)	Closed	192	179
AN (dry)	Open	188	190
AN/H ₂ O (10% H ₂ O)	Closed	214	217
AN/H ₂ O (20% H ₂ O)	Closed	217	225
AN/H ₂ O (10% H ₂ O)	Open	203	201
AN/H ₂ O (20% H ₂ O)	Open	204	210
AN/SN/SP (dry)	Closed	180	184
AN/SN/SP (dry)	Open	170	181
AN/SN/SP/H ₂ O (13% H ₂ O)	Closed	215	221
AN/SN/SP/H ₂ O (13% H ₂ O)	Open	199	208

In the case of open AN, AN/SN/SP, and ANS systems, the ARC (3 g) Arrhenius plots are generally much more linear than for the corresponding closed systems. This is shown in Fig. 14 (top) for dry AN in open system. In a closed system, the initial rate of runaway in the ARC is usually faster. This is also shown in Fig. 14 (bottom) for an AN/water (90/10) solution in a closed system. As discussed in Section 4.1, this clear decrease in rate after the initial stage of runaway may be caused by the evolution of water vapor and ammonia out of the sample, which are both known to suppress the rate of AN decomposition. Due to the much larger scatter in the ADC data near T_o and to the larger free volume of the Dewar, this effect is generally not observed in the ADC data.

From Fig. 14, it is also seen that, if only the initial part of the ARC (3 g) exotherm is used in the extrapolation, consistent extrapolated T_o values are obtained with the two calorimeters for these systems. The results of such extrapolations for all the AN and ANS systems investigated in both calorimeters are presented in Table 4. It is seen that, when using this procedure, the ADC and ARC (3 g) extrapolated results are consistent to within about 10 °C, in all cases. Such differences are expected, as the precision of the ARC extrapolation is much lower than for the ADC. Not only the ϕ correction is much more important in the former case, but also, as pointed out in Section 2.4, the effective ϕ for the ARC is a rapidly varying function of the sample mass and heat capacity, for a fixed mass of the sample vessel.

In the absence of any oil phase the results obtained in the present work demonstrate that ARC experiments can be used to obtain realistic onset temperatures for large storage or transportation quantities of AN-based oxidizers and oxidizer solutions. Adequate safety margins for these systems can be obtained by using the lowest extrapolated value of Table 4 and by subtracting 20 °C from this value. This additional safety measure is necessary to allow for long residence times.

When an oil phase is present in the system, an extrapolation such as the one referred to above is clearly not possible due to the large differences in initial free volume for the two calorimeters. More work, involving the identification of early AN dissociation products, will be required to better understand the reaction between the oil phase, air, and AN and to generate safe and conservative maximum process temperatures for AN-based explosives.

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