ELSEVIER Thermochimica Acta 331 (1999) 37–44

thermochimica acta

Parameters affecting the thermal behaviour of emulsion explosives

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Received 17 June 1998; received in revised form 24 November 1998; accepted 28 November 1998

Abstract

There have been numerous international instances over the last several years in which pumping of an emulsion explosive has resulted in an accident. To address the sensitivity of emulsion explosives to various parameters including pressure, a study of a particular ammonium nitrate (AN) based emulsion explosive has been undertaken using the ARC (accelerating rate calorimeter) and a Tian-Calvet heat flux calorimeter (HFC).

The effects of pressure and both inert and oxidizing atmospheres on thermal behaviour were determined and compared with similar results obtained for AN per se. All the results for the emulsion explosive suggest an increased thermal hazard when operating in air in contrast with the observations for the same measurements in Argon. No such difference in the results for AN in air and Argon was observed.

Significantly lower onset temperatures are observed in air from both the ARC and HFC measurements on the emulsion explosive. This observation is believed to be the result of oxidation of the oil phase in the emulsion. Additionally, the ARC results show some dependence on the choice of the initial temperature; a lower initial temperature results in an elevated onset temperature. Sample size also appears to be a factor influencing the onset temperature for both the HFC and ARC results.

At a heating rate of 0.1°C min^{-1}, the HFC results show a complex exotherm pattern for the emulsion in both Argon and air, but the latter results give a decidedly earlier onset temperature and a slightly larger ΔH. A complex exotherm pattern is expected for the decomposition of AN but, for the emulsion in air, oxidation of the oil phase further complicates the result.

Keywords: AN; Emulsion explosives; HFC; ARC

1. Introduction

Emulsion explosives are in increasing use at this time because of the advantage that they offer over ANFO (ammonium nitrate-fuel oil) and slurry explosives. In spite of their relatively high cost, they have significant benefits such as improved water resistance. Recently, heavy ANFO [1] has been formulated with AN-based emulsion explosive filling in the voids between the prills of ANFO, at very little extra cost. It has become common practice to pump these explosives during their manufacture, transfer or loading into boreholes. Two major Canadian and several international accidents [2] have resulted from pumping emulsion explosives.

Perlid has carried out extensive safety tests using a variety of emulsion explosives in a progressive cavity pump in a circulation system against dead head and under dry pumping conditions. He showed that dry

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PII: S0040-6031(98)00660-1

pumping, a heavy ANFO product, resulted in rapid temperature increase over 800°C, with destruction of both the product and the rubber parts in the pump. When a cap-sensitive emulsion explosive was used under the same conditions, an explosion occurred, damaging the pump and the tubing in the system.

The thermal behaviour of an emulsion explosive is a key property that affects sensitivity and ultimately its safe use. The parameters that determine thermal behaviour are therefore of significant importance. Olson [3] has shown that an increase in initial temperature in an emulsion matrix lowers the minimum burning pressure and raises the linear burning rate.

In Canada, a pumping consortium has been formed for the purpose of focussing on safety issues related to the pumping of explosives. As part of our contribution to this effort, the Canadian Explosives Research Laboratory (CERL) has undertaken, in cooperation with local industry, experimental work aimed at elucidating factors that affect thermal properties of emulsion explosives.

2. Experimental

The emulsion explosives were received from ETI Explosives and used without further treatment. Ammonium nitrate (AN) with a purity of 99% was purchased from Baker.

A heat flux calorimeter (HFC) and an accelerating rate calorimeter (ARC) were used to examine the thermal properties of AN and the AN-based emulsion explosives.

2.1. HFC

The calorimeter, manifold and special high pressure vessels were used as described in [4]. The following two methods were used for loading samples in the HFC: (1) the samples were added directly into the high pressure vessel and the pressure change was read by a pressure transmitter during the experiments. In this way, experiments were carried out at ambient and 5.4 MPa pressure of air and argon. In this method sample size varied from 0.1 to 1.0 g, and (2) the samples were sealed in a glass ampoule which had an internal volume of about 0.7 cm^3. The glass ampoule was loaded in the high pressure vessel and a helium gas environment was used to provide good thermal conductivity. Sample size was less than 0.1 g. Heating rates for all experiments were between 0.1 and 0.3°C min^{-1}.

2.2. ARC

The ARC is a commercial automated adiabatic calorimeter distributed by Arthur D. Little and used for the purpose of assessing the thermal hazard potential of energetic materials [5]. Adiabatic conditions are maintained in the ARC provided that the rate of temperature increase does not exceed about 10°C min^{-1}.

Samples of 0.5 g AN and 0.5 and 2.0 g of AN-based emulsion explosive were placed in spherical vessels which were closed in order to maintain any pressure resulting from vapourization or decomposition of the sample. Experiments were carried out in dry air, after the closed system had been tested for leaks and adjusted to an initial pressure, P_{initial}, from 0.1 to 4.0 MPa. The sample was heated quickly to a pre-selected initial temperature, T_{initial}, equilibrated at that temperature for a period of time and subsequently subjected to the standard ARC procedure of ''heat–wait–search''; the temperature of the system was raised to 5°C and the system was maintained adiabatic both during periods of dissipation of thermal transients and of ''search'' for an exotherm, defined as a self-heating rate R, exceeding 0.02°C min^{-1}. The temperature at this rate is a measure of the onset temperature, T_0 for decomposition, although exotherms are not detected during the ''heat'' or ''wait'' modes.

Whenever $R \geq 0.02$°C min^{-1} (detected during the ''search'' mode), the ''heat–wait–search'' procedure is automatically interrupted, but collection of time, temperature and pressure data continues. Data collection was programmed to stop in the event that some other pre-selected condition was exceeded. For example, experiments using 2.0 g of emulsion explosive were programmed to shut down when $R > 1$°C min^{-1}.

Thermal hazard studies using the ARC have been published [6,7] and the thermokinetic information that can be obtained from ARC measurements has been described previously [5]. In this work, two sets of conditions (Table 1) were used for the different phases of the program.

Table 1
Experimental parameters used in ARC measurements

Mass (g)		Step heat/°C	Wait time/min	P_{initial}/MPa	T_{initial}/°C
Sample	Vessel				
0.5	10 (titanium)	10	20	1.0	50
0.5, 2.0	40 (Hastelloy C 276)	5	60	0.1–4.0	100, 130, 150

3. Results and discussion

3.1. HFC

3.1.1. High pressure vessels

The experimental curves for AN and an emulsion explosive in argon are compared in Fig. 1. From this Figure, the four phase transitions observed for AN disappeared in the emulsion explosive. In fact, observation of crystalline phase transition in an emulsion explosive is not a good sign since this suggests crystallization of AN, thereby altering the performance of the explosive. The onset temperature for AN appears to be lower than that observed for the emulsion explosive whereas the rate of the reaction for the emulsion explosive is significantly faster than that for AN. A shoulder was observed in the high temperature region of the exotherm for the emulsion explosive, indicating a complex reaction mechanism.

The results for AN at ambient pressure of air and 5.4 MPa of both air and Argon are shown in Fig. 2. The peak temperatures of the exotherms in the high pressure measurements were shifted to slightly higher values.

The experiments for the emulsion explosive were carried out at ambient pressure of air and 5.4 MPa of air and Argon. All these results are shown in Fig. 3. Firstly, comparing the results obtained at ambient pressure of Argon and air, it is found that the real onset temperature for emulsion explosives at ambient pressure of air is lower than that at ambient pressure of Argon by about 15°C. The peak temperature is also shifted to a lower temperature by about 15°C. These results suggest that early oxidation takes place in experiments conducted in air. From Fig. 3, even lower

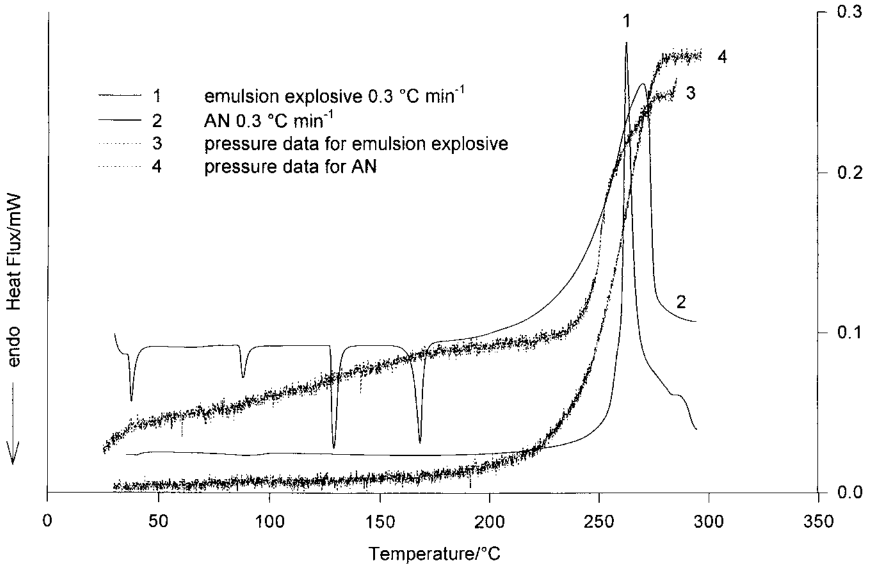

Fig. 1. Comparison of HFC results for AN and emulsion explosive.

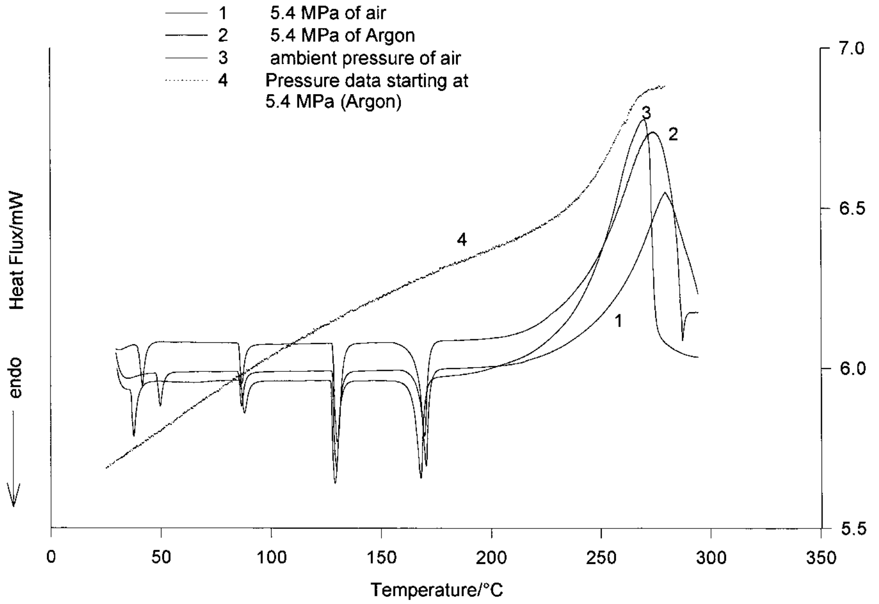

Fig. 2. Effect of pressure on HFC results for AN.

onset temperatures were observed from the results at 5.4 MPa of air and the exothermic reaction is broader, more complex and incomplete at 300°C. High pressure of inert gas inhibited the exothermic reaction of the emulsion explosive. Clearly, for the experiments carried out at 5.4 MPa of air, two factors affect the thermal behaviour of the emulsion explosive: oxidation and inhibition. The former tends to lower the onset temperature whereas the latter tends to delay subsequent reactions.

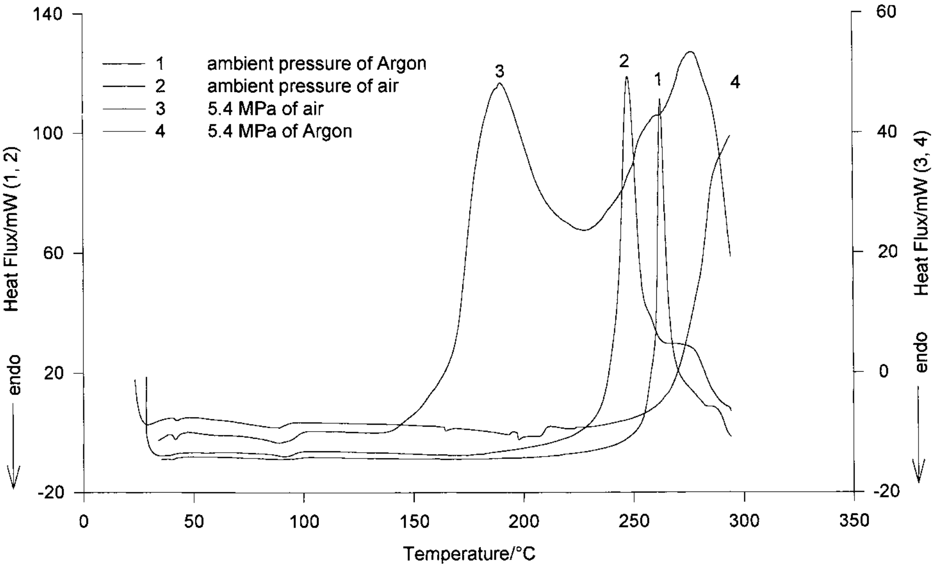

Fig. 3. Effect of pressure and gas environment on HFC results for emulsion explosive.

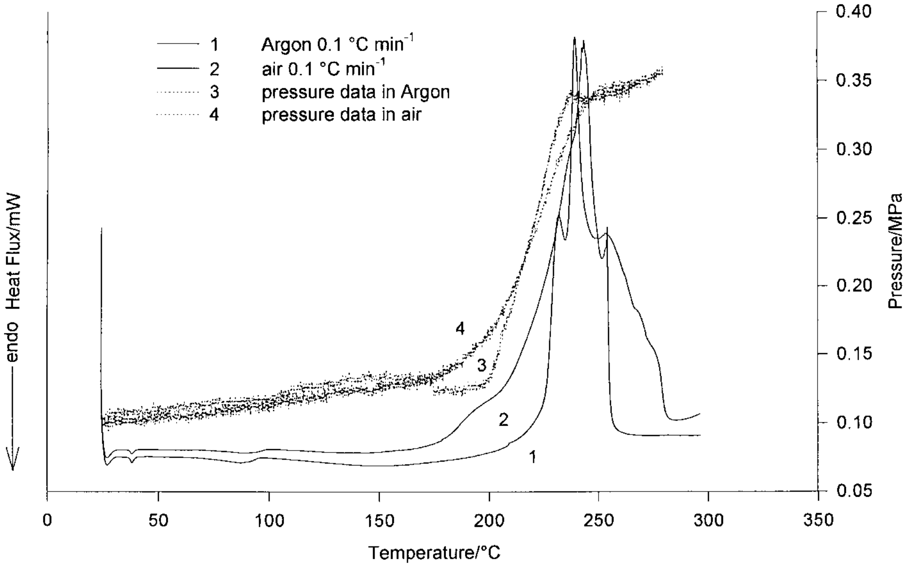

Fig. 4. HFC results for emulsion explosive in Argon and air at 0.1°C min^{-1}.

Experiments were also carried out at a heating rate of 0.1°C min^{-1} in order to obtain the entire exothermic peak. The results obtained at ambient pressure of air and Argon are shown in Fig. 4. The entire peaks were obtained for both conditions. Similarly, early oxidation and lower onset temperature of the exotherm were obtained from the results at ambient pressure of air. When 1 g of the emulsion explosive was used, ignition took place in both air and Argon at ambient pressure conditions. These results are shown in Fig. 5.

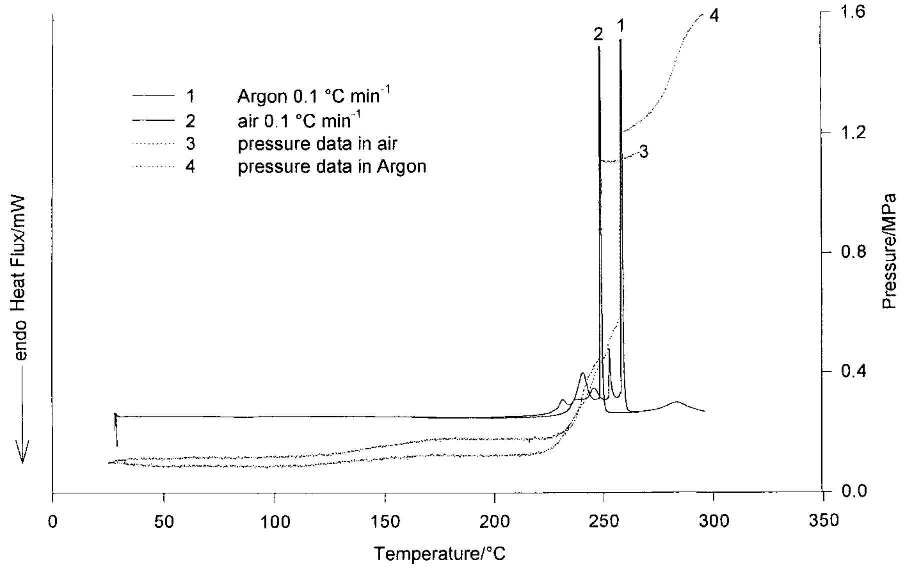

Fig. 5. HFC results using 1 g emulsion explosive.

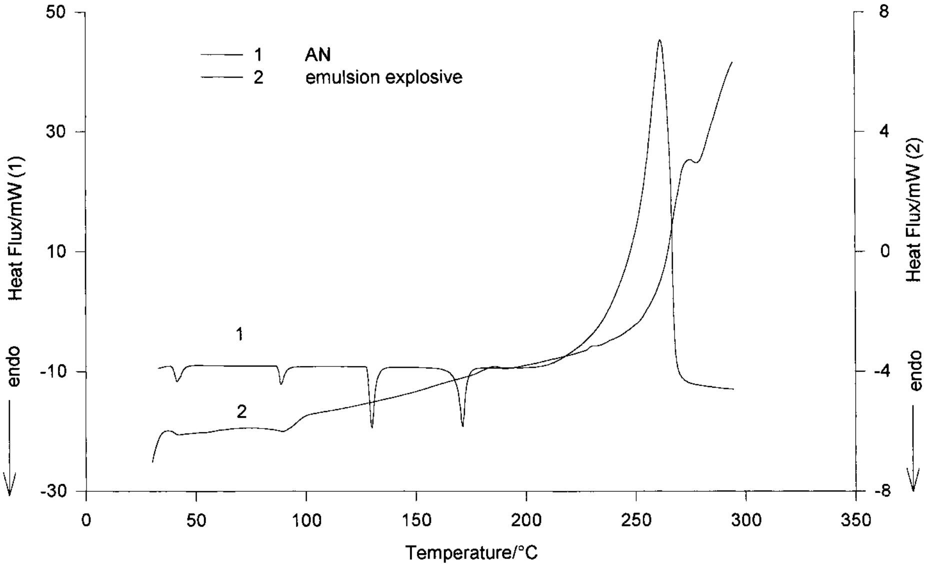

Fig. 6. HFC results for AN and emulsion explosive loaded in glass ampoules.

At least three peaks were found in the thermogram at ambient pressure of air and the ignition temperature is lower than that at ambient pressure of Argon, in which at least four peaks were observed. Self-heating was considered as the reason for ignition in the larger sample sizes.

3.1.2. Ampoules

The samples were directly loaded into the high pressure vessel in all the above experiments. Because the manifold has a larger free volume than that of the vessel, part of the sample might have vapourized and condensed in the manifold during the experiments. In the experiments, the results of which are described below, the sample was sealed in air in a glass ampoule in order to avoid material loss and also to simulate a confined condition. All the results are shown in Fig. 6. The results for AN show the complete exotherm and a higher rate of reaction, compared with the results from AN obtained using the high pressure vessel. Surprisingly, the results for the emulsion explosive indicate delay of onset temperature by about 50°C, similar to the results obtained using high pressure of inert gas. This suggests that an increase in pressure from inert products, such as water, is inhibiting the exothermic reaction. The residual of this sample was re-run and the exothermic reaction appeared again, indicating that the reaction was incomplete in the first cycle.

Table 2
ARC results for emulsion explosives

Sample/run	T_0/°C	P_0/MPa	At maximum (m) rate			
			T_m/°C	P_m/MPa	R_m/°C min^{-1}	t_m/h
1/1	182	1.8	349	6.8	>10	8.3
1/2	175	1.8	375	8.7	2.5	8.1
1[a]	272	1.2	370	5.2	10	2.8
2/1	204	1.9	358	12	>10	21
2/2	192	1.8	367	11	>10	19
AN[a]	217	0.68	242	2.4	0.2	4.0

[a] Starting at ambient pressure P_0 at onset temperature T_0.

Table 3
ARC results for emulsion explosive

Mass/g	T_{initial}/°C	P_{initial}/MPa	Exotherm 1			Exotherm 2			
			T_0^{ext}/°C	R_m/°C min^{-1}	ΔP_1/MPa	T_0^{est}/°C	R_m/°C min^{-1}	ΔP_{1+2}/MPa	$10^2(\mathrm{d}P/\mathrm{d}t)_m$/MPa min^{-1}
0.5	150	0.70	150	0.06	2.9	252	0.51	6.5	1.8
		1.46	168	0.04	1.8	260	0.26	4.4	1.9
		2.59	155	0.10	1.5	236	0.5	5.0	3.4
		3.99	150	0.16	1.3	246	1.8	>5.7	16
	100	0.10	230	–	(0.4)	235	0.06	3.8	0.6
		0.46	215	0.08	1.9	236	0.47	5.6	4.0
2.0	130	0.10	–	–	(0.4)	218	>1	>2.2	5.4
		1.37	195	0.02	0.2	224	>50	>3.2	28
		3.13	135	0.03	0.0	165	>1	>2.3	6.6
	150	1.43	175	0.08	1.2	220	>1	>4.2	6.6

ext: extrapolated to R=0; est: estimated; ΔP_1: estimated pressure increase during Exotherm 1; ΔP_{1+2}: total pressure increase during both exotherms; $(\mathrm{d}P/\mathrm{d}t)_m$ is the maximum rate of pressure rise.

3.2. ARC

Table 2 lists the ARC results obtained for earlier studies on two emulsion explosive products, sample 1 having less AN and more calcium nitrate (CN) than sample 2. It is clear that onset temperatures, T_0 are lower for emulsion explosives at P_{initial}=1.0 MPa than at ambient pressure and also lower than the onset temperature for AN. Onset temperatures for AN and emulsion explosive at ambient pressure show the opposite behaviour.

In a more recent study, a Hastelloy C vessel was used, in spite of its larger mass and lower sensitivity, because there was some independent evidence for a catalytic effect in titanium vessels. A compilation of all the results for two sample masses, at a series of initial temperatures and pressures is given in Table 3. The composition of this emulsion explosive is similar

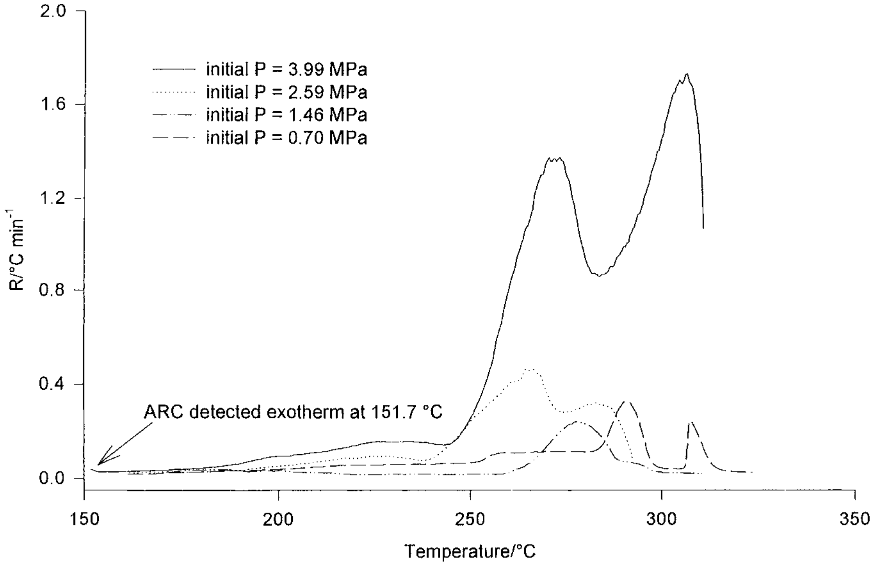

Fig. 7. ARC results for emulsion explosive at a series of initial pressures.

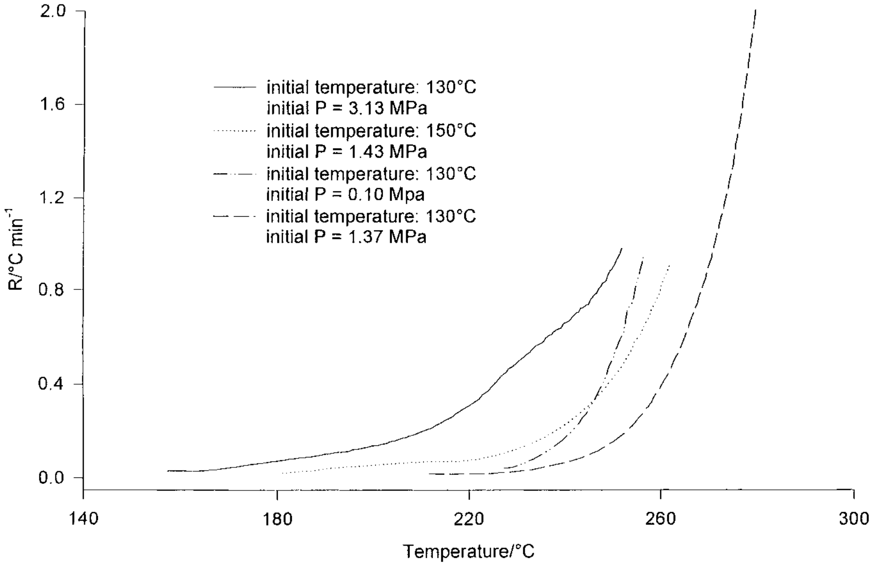

Fig. 8. ARC results for emulsion explosive at a series of initial temperatures and pressures.

to that of sample 2 in Table 2. Table 3 and Figs. 7 and 8 indicate that both rates dT/dt (R) and dP/dt generally increase as the initial pressure increases. This behaviour is also observed for AN per se [8]. Additionally, the initial temperature, T_{initial}, seems to determine whether or not the first exotherm is detected so that at 100°C (Table 3) it is not commonly detected. From Fig. 8, it appears that the onset temperature decreases with increasing pressure, although there is no such pattern from the results in Table 3 for 0.5 g of emulsion at T_{initial}=150°C. Finally, it is apparent that the highest rate in all the tests occurs at the highest initial pressure.

From a comparison of the results in Tables 2 and 3, it appears that a lower initial temperature results in a higher onset temperature but also generally leads to a runaway reaction ie R_{m}>10°C min^{-1}.

4. Conclusions

The exothermic reaction for AN is not affected by the nature and pressure of the gas environment. In contrast, the exothermic reaction for emulsion explosives is dependent on the gas environment. Oxidative decomposition of the oil phase in the emulsion explosive in air is observed. High pressure of inert gas tended to inhibit and delay the exothermic reaction for emulsion explosives. But in air oxidative decomposition resulted in a lower onset temperature with a decomposition, broadened by the effect of the high pressure.

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