

## Chapter 7

### Experiments on the interaction of self-heating drums.

#### 7.1. Introduction

From consideration of the previous chapter, it is clear that the experimental determination of the critical ignition temperature of a normally loaded freight container of hydrated HCH is the definitive method for determining the 'safe' maximum temperature at which this substance can be stored or transported. However, there is no mention in the open literature of this having been done.

Bowes (1984) has attempted to estimate the critical ignition temperature CIT of freight container quantities of the anhydrous form of HCH using the usual Frank-Kamenetskii (1969) extrapolation of experimental CAT data. Due to the previous lack of experimental data, similar predictions regarding hydrated HCH have not been published. This simple method, while useful in providing some general information regarding the CIT of the assembly in question, does not account for the local internal convectional environment (common airspace) or the complex nature of heat transfer within and through the freight container. Given the sensitivity of this material to the local convectional conditions discussed in chapter 6, it is imperative to approximate the complex heat balance and heating behaviour within the freight container if an accurate prediction of the CIT is to be made. These aspects have not been pursued experimentally and are hence the focus of this current chapter.

While Boddington et al has examined the self-heating problem where thermons are contained within a heat bath of limited heat capacity with respect to the storage and transport of propellants, this problem only recently been examined from the perspective of transport within standard shipping containers. The model of Gray (2000) represents a new attempt to accurately account for the complex heating phenomenon that occurs when individual containers of a self-heating substance, which Gray calls 'thermons', are packed within a larger container of finite heat capacity. Furthermore, using the kinetic

and thermodynamic parameters discussed in the previous chapter, Gray has applied the model to the packing arrangements of HDPE and fibre drums filled with hydrated HCH that are typical of the configurations found within loaded shipping containers of this material.

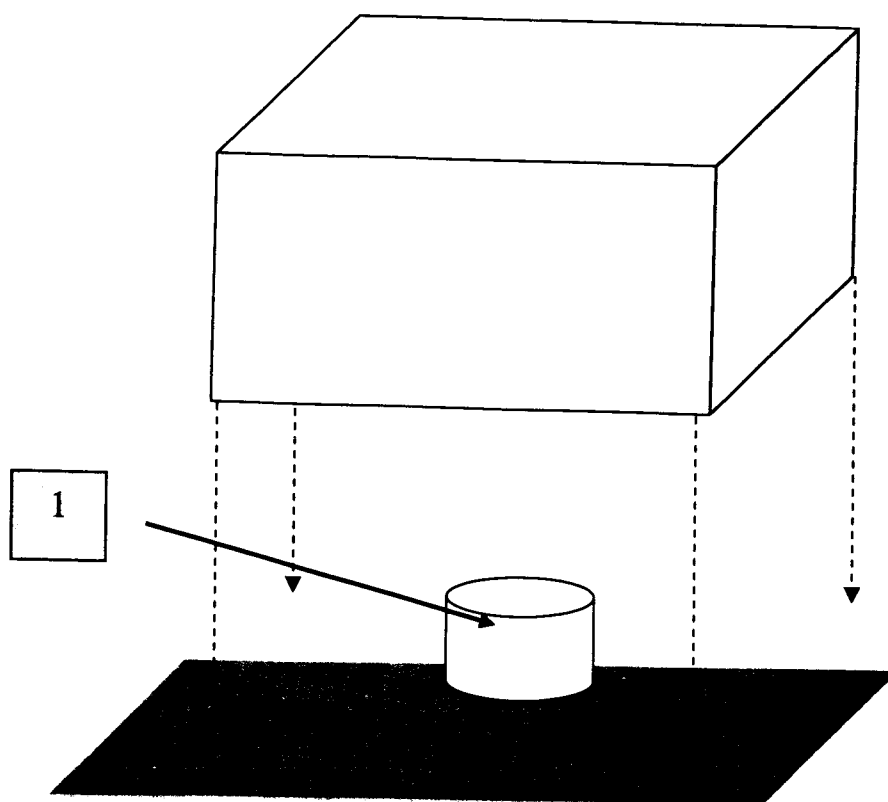
Packing a large number of drums of a self-heating substance into a freight container can, for materials with a low Biot number, result in a different heat transfer regime than that of a single drum. Consider the case typical of sea transport of this material, where in one standard 6m long freight container, 80 x 200kg drums of hydrated HCH were stacked 2 drums high. In this case, each individual drum was closely packed within the common airspace of the fully packed freight container, but separated from the exterior air by a thermal barrier that consisted of steel walls and a timber floor of the freight container. With this configuration, two types of behaviour are possible depending upon the balance of the rates at which heat enters and leaves the common airspace. If the freight container exhibits little or no thermal resistance, then the rate of heat removal from the common airspace will at all times exceed the rate of heat entry. For this case, the CIT of the assembly will be identical to that of an individual drum. Conversely, if the freight container exhibits a finite thermal resistance, then the possibility exists for the rate of heat entering the common airspace to exceed the total heat loss rate through the walls of the container, thereby accumulating heat within the common airspace. For this condition, the local air temperature experienced by each drum will clearly not be the same as the air temperature exterior to the freight container. Given the above situation, the CIT displayed by the entire assembly will be less than that of an individual 200kg drum. Hence, to accurately estimate the CIT of the entire assembly, the total heat balance within the common airspace will need to be taken into account.

The work described in this chapter experimentally examines the model of Gray (2000). The experiments described in this chapter are aimed at verifying the ideas and assumptions of Gray's (2000) model. Two CAT's are examined, the CAT of an assembly consisting of 18 drums of HCH packed into a steel box and the CAT of a single, but identical, drum placed into the same steel box. In all experiments discussed in this chapter, the apparatus described in chapter 5 has been used

(SADT modifications completed) in conjunction with a 14kg HDPE sample drums with lid (0.135m radius and a height of 0.27m). The 14kg drums were also loaded and instrumented as described in chapter 5. It should be noted, however, that the entire ensemble (14kg drum contained within the steel box) was placed into the large oven discussed in section 5. Hence, the only experimental difference between the experiments discussed in chapter 6 and the experiments discussed in this chapter is that the sample drums are surrounded by a steel shell. The drums were completely filled with sample so that when the lid was pressed in place, intimate contact was made with the HCH sample. Throughout all experiments, individual hydrated HCH samples were taken from the same batch of HCH. The CAT's measured during this current study are also compared to the SADT test on an identical 14kg drum. The CAT values reported in this chapter are generally a result of several individual measurements, however, for clarity, only the most precise two measurements that bracket the reported CAT are displayed, that is, the minimum temperature at which critical behaviour is displayed and the maximum temperature at which sub-critical behaviour is displayed. All data plots have been displayed with a reduced data set for presentation purposes with all data recorded to at least 1 minute time intervals.

## **7.2. Determination of the CAT of a single 14kg HDPE drum of hydrated HCH using conditions of natural convection**

The aim of the first set of measurements was to determine the CAT of a single 14kg drum of HCH using the same heating environment as that to be used for the second part of this study, the 'interaction' experiments. A steel box with a wooden floor of dimensions 0.95m x 0.95m x 0.64m was used to enclose the loaded and instrumented 14kg HDPE drum of HCH. The steel box was of a capacity that would allow the close stacking of 18 of the 14kg drums, thus providing identical heating conditions for both the current single drum measurements and the later interaction experiments. For the current measurements, a single 14kg HDPE drum was placed in a middle position, position '1' as shown in figure 7.2.1.



*Figure 7.2.1. An exploded view of the single 14kg drum of hydrated HCH showing the positions of the instrumented containers.*

The results for CAT measurements upon the single 14kg drum of HCH are displayed figure 7.2.2.

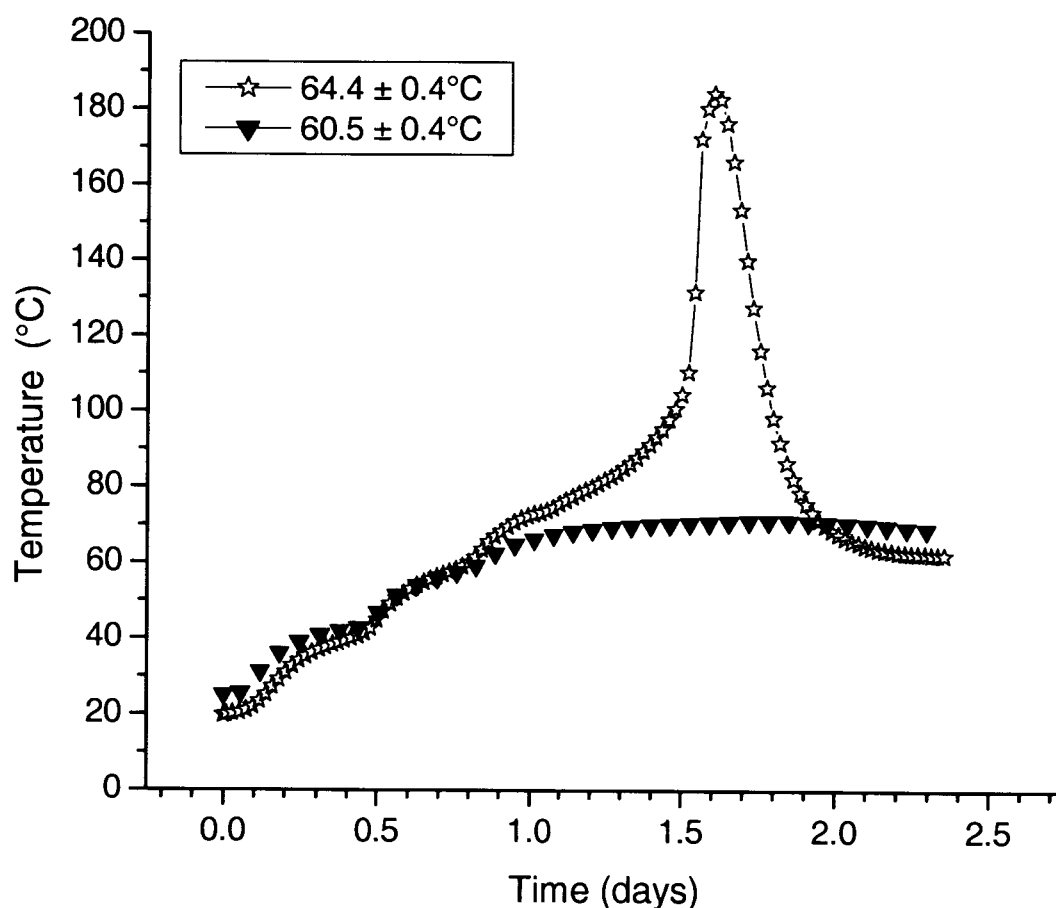
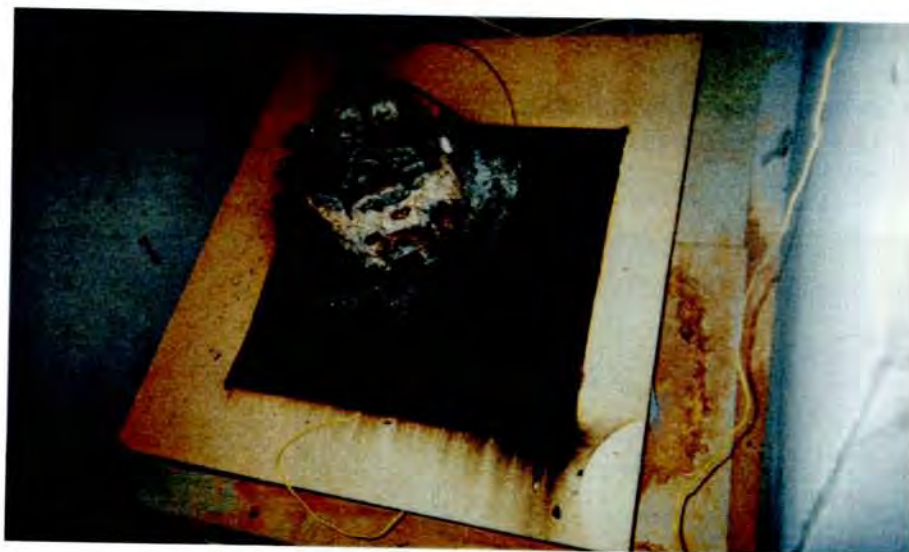


Figure 7.2.2. Sub-critical and super-critical temperature time traces for a single 14kg HDPE drum using conditions of natural convection. .

These data in figure 7.2.2 display the usual divergence between sub-critical and super-critical self-heating behaviour. The measurement displaying super-critical behaviour was completed at an oven temperature of  $64.4^\circ\text{C} \pm 0.4^\circ\text{C}$  while the sub-critical run was completed at  $60.5^\circ\text{C} \pm 0.4^\circ\text{C}$ . The CAT for this series of measurements was calculated in the usual manner to be  $62.5^\circ\text{C} \pm 2^\circ\text{C}$ . In figure 7.2.2 both of these traces exhibited unusual heating behaviour between  $40^\circ\text{C}$  and  $50^\circ\text{C}$ , suggesting that at least one endothermic process is occurring over this temperature range. This feature was also seen in the 40kg CAT measurements described in chapter 6, although this feature appears to be more pronounced at this size. While the data displayed in figure 7.2.2 show the CAT measurements for the container at position 1, a measurement was also completed with the container suspended above position 1. This measurement also displayed super-critical behaviour at an ambient temperature of  $64^\circ\text{C}$ .

The CAT values measured in this current work were found to be significantly lower than the expected value of 73.5°C that was determined by the usual interpolation of the Frank-Kamenetskii (1969) plot using the high temperature data. Initially it was thought that this current sample, which was from a separate batch to the sample used in chapter 6, was more reactive. This, however, proved not to be the case. A series of comparative basket experiments and chemical analysis of the sample revealed no significant difference between the two batches. Since the only detected difference between the current experiments and the experiments from chapter 6 was the degree of filling it was deduced that the level of filling was the most probable cause of this anomaly. While all of the commercial containers used in chapter 6 possessed an airspace between the surface of the sample and the lid when filled, this was not the case for the current investigation where each container was completely filled with sample. Given that the surface to volume ratio and the heat transfer regime within a completely filled drum would not be expected to be identical to that of a partly filled drum, this result is not unexpected. This anomaly, however, requires further investigation, as the precise mechanism by which the removal of the ullage from each container resulted in a lowering of the CAT, is not understood. While further investigation is required to correctly account for this phenomenon, it makes no impact upon the outcomes of this current work as comparisons in CAT values are made with an identically filled container.

Figure 7.2.3. shows a view of the remains, from inside the oven, of the sample following the super-critical measurement. The view is slightly to one side of overhead. The image was photographed following the removal of the steel box.



*Figure 7.2.3: The remains of the 14kg HDPE container inside the oven, following the super-critical experiment. The centrally located thermocouple wire is also shown. The black deposits on the wooden floor are a combination of both charring and soot deposit.*

Notice that ignition and complete combustion of the HDPE container has occurred in this case. This example clearly illustrates that while super-critical thermal heating of HCH in isolation will not produce flames, this is not the case when this substance is contained within combustible containers, where the thermal rise of the HCH is sufficient to ignite the container. Notice also of the charring of the wooden floor, the soot deposits resulting from the charring and the scorch marks radiating away from the where the bottom edge of the box was positioned. This figure also shows that while the steel box sitting on a wooden floor is not strictly airtight, little mixing between the oven air and the air within the box occurs.

### **7.3. Determination of the CAT of an assembly of 18 x 14kg HDPE containers of hydrated HCH using conditions of natural convection**

This series of measurements aims to investigate whether the CAT of a 14kg container of hydrated HCH is altered as a result of placing 18 of such containers into a heat bath of finite thermal capacity.

The assembly used consists of two layers, with each layer comprising 9 containers with the whole ensemble is contained within a steel box. The packing assembly of the 18 x 14kg HDPE hydrated HCH containers is shown in figure 7.3.1.

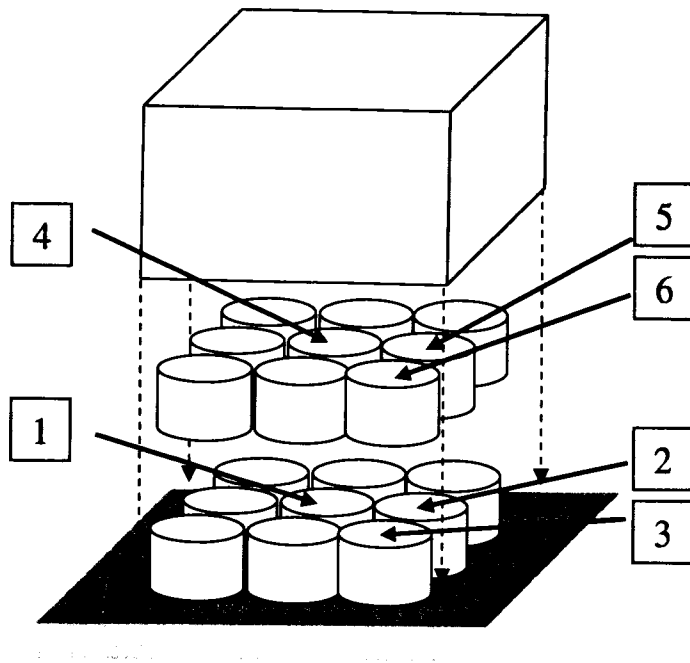


*Figure 7.3.1: The assembly of 18 x 14kg containers of hydrated HCH. Two of the upper layer containers are yet to be positioned.*

As can be seen in the above figure, the containers are not cylinders. The containers taper from an upper internal diameter of 0.257m to a base diameter of 0.232m over a height of 0.230m. A 2cm recess is manufactured into each lid that allows the base of one container to fit snugly into the top of another when stacked vertically. When stacked two high, the position of maximum distance from any external surface is located just below to the lid of the lower container and has a diameter 12mm larger than the diameter at the position of the thermojunctions that were embedded into the centre of each container.

Figure 7.3.2 shows an exploded view of the assembly. The containers instrumented with thermojunctions sensors are shown and are labeled. The illustrated numbering code will be used throughout this chapter to identify the instrumented containers.





*Figure 7.3.2: An exploded view of the assembly of 18 x 14kg containers of hydrated HCH showing the positions of the instrumented containers.*

A thermojunction was also positioned between the lid of the container located at position 1 and the base of the container located at position 4, that is, at the centre of the interface where the base of the container located at position 4 slots into the lid of the container located at position 1. It should be again noted that the drums were completely filled and no air space existed between the HCH contained within the upper and lower drums. A further thermojunctions was located in the air approximately 1cm above the centre of the container located at position 4. This position was approximately midway between the upper surface of the container located at position 4 and the top surface of the box. This thermocouple was used to measure the temperature of the air within the top section of the box. Additional thermocouples were located between the containers located at position 1 and 3, 4 and 6, 3 and the box and 6 and the box. In the case of the thermocouple located between the containers located at position 1 and 3, these was positioned vertically at approximately the half height of the drums in question and and midway between them horizontally. The thermocouple located between the containers located at positions 4 and 6 were similarly positioned at approximately the half height of

the containers located at position 4 and 6 and midway between them horizontally. The thermocouple located between the container located at position 6 and the inner surface of the box was positioned vertically at approximately half the height of the container located at position 6 and midway between the container located at position 6 and the inner surface of the box. The thermocouple located between the container located at position 3 and the inner surface of the box was again similarly positioned vertically at approximately the half height of the container located at position 3 and midway between the vertical surfaces of the container located at position 3 and the inner surface of the box.

The assembly with the steel box in place is shown in figure 7.3.3.



*Figure 7.3.3: The assembly of 18 x 14kg containers of hydrated HCH with the steel box in position. Due to the close proximity (100mm) to the oven walls, 12 thermojunctions were placed about the box to determine ambient temperature; some of these can be seen in this figure.*

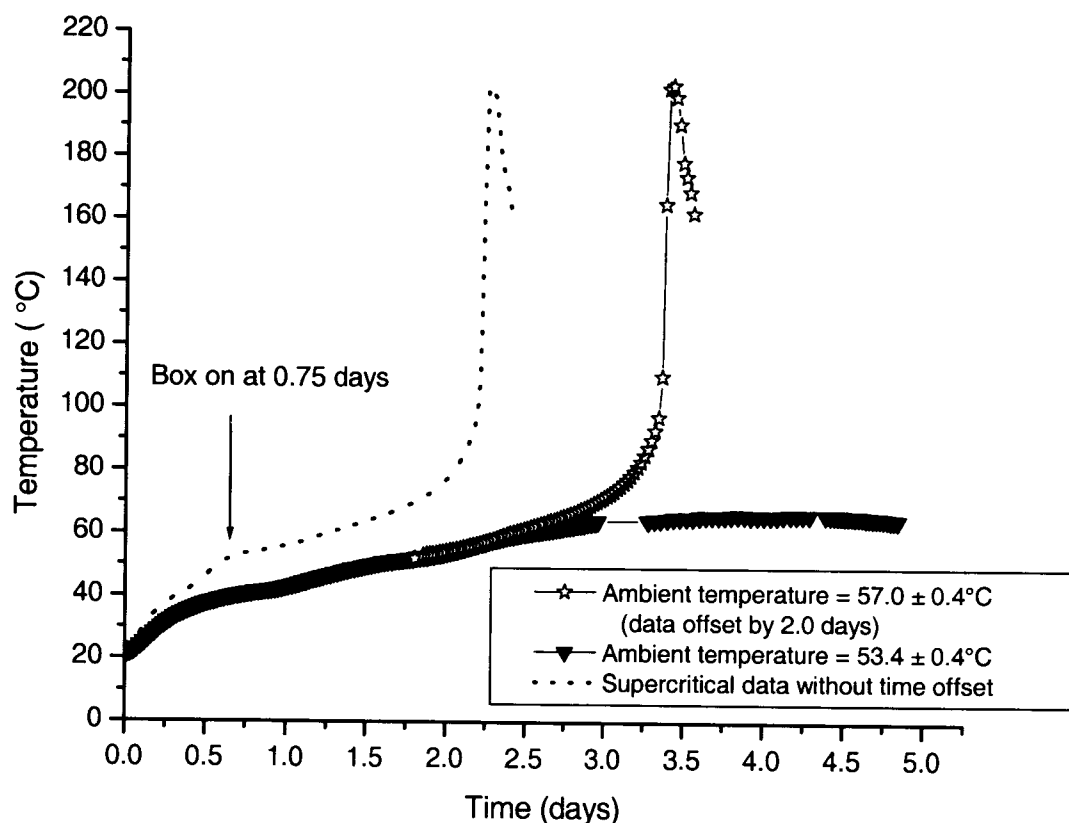


Figure 7.3.4: Sub-critical and super-critical temperature time traces for the container located at the middle position of the upper layer of the assembly containers. The dotted line shows the original heating profile of the super-critical run.

While the sub-critical assembly of containers experienced conditions of natural convection for the entire duration of the experiment, this was not the case during the super-critical measurement where the assembly was initially heated without the box, for the first 18 hours. This modification was undertaken because of time constraints to complete these measurements quickly. Since that  $E/R$  is large for HCH, it can be reasonably assumed that reactant consumption during the warm up stage is negligible (Bowes, 1984. page 187). Hence, it can be assumed that this modification would have negligible effect on the behaviour of the HCH.

In comparing the results of these two sets of data, it was assumed that the different convective heating environment prior to the sample reaching ambient oven temperature, would not significantly impact upon the displayed thermal ignition behaviour of each sample. Hence, the results of these two experiments have been directly compared. Additionally, the box was placed over the assembly approximately 0.75 days before reaching ambient oven temperature. Given that the thermal lag (or the time delay, as a result of the thermal inertia of the HCH sample) between the centre of each drum to a surface temperature change was of the order of 30 minutes, it was expected that the self-heating behaviour displayed by the drums heated at an increased rate would not be significantly different to drums that were heated entirely within the box. Hence, for the presentation and comparison of the data, the super-critical data in figure 7.2.3 has been displayed in both the original form, with the initial warming under forced convection, and with the time scale offset by 2 days, which was the time required for the sub-critical measurements to heat to 53°C. The combination of natural convection in conjunction with the increased thermal resistance of the box, have clearly extended the induction time by approximately 280% compared to the forced convection case. Also, and most importantly, these conditions have reduced the critical temperature for this assembly by 7 °C to  $55.2^{\circ}\text{C} \pm 2^{\circ}\text{C}$ .

Figure 7.3.5 shows the temperature time history of the drums located at positions 1 to 6 in figure 7.3.2 at well as the temperature at the interface between the containers at positions 1 and 4. The ambient temperature of  $57.0^{\circ}\text{C} \pm 0.4^{\circ}\text{C}$  is also included. This figure is included providing the reader with an overview of the thermal ignition sequence; individual detailed aspects of these data are discussed in subsequent figures. In interpreting these data, it should be again noted that the drums were completely filled and no air space existed between the HCH contained within the upper and lower drums.

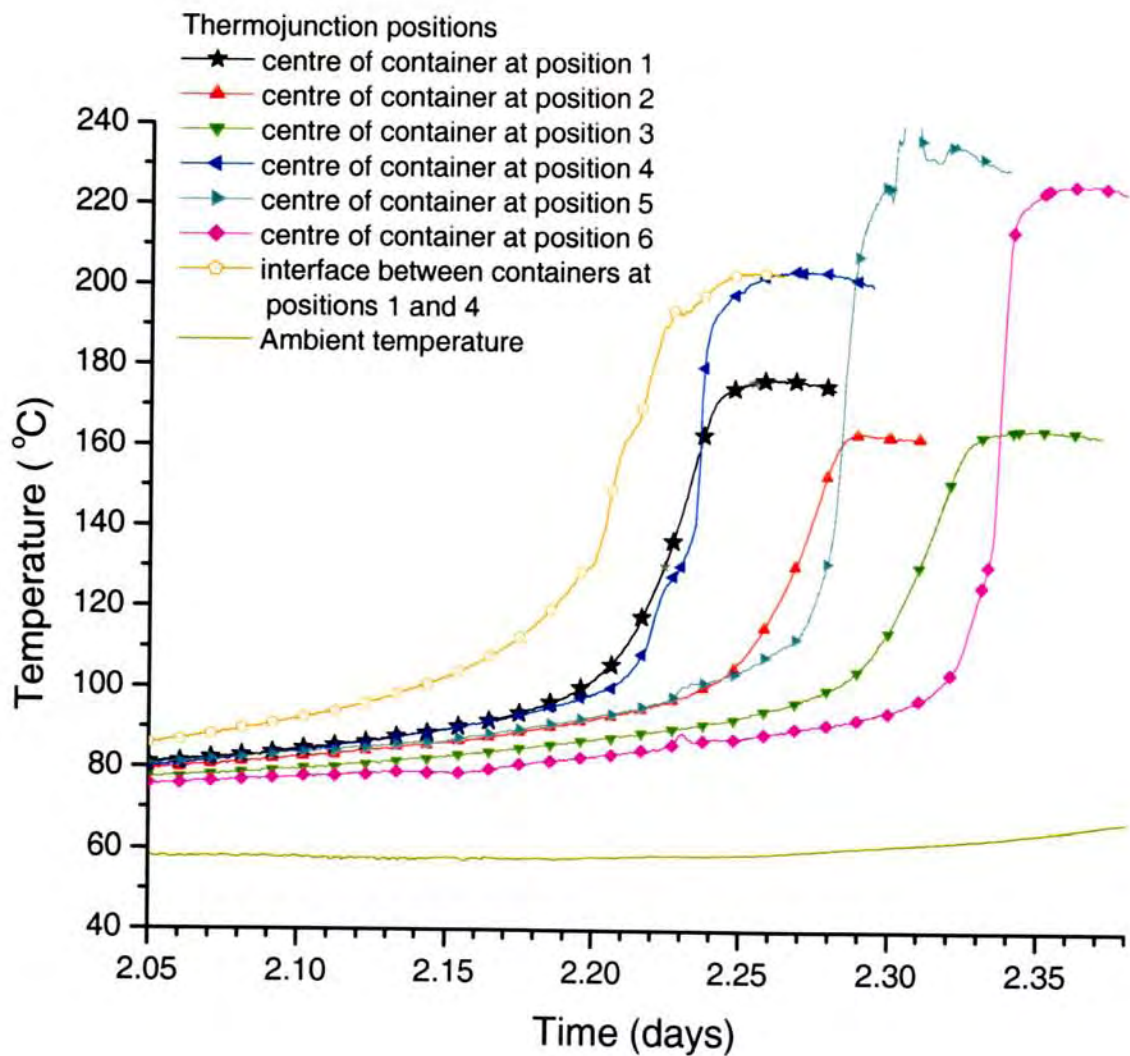


Figure 7.3.5: Super-critical temperature profile of the containers located at position 1 to 6 and the air temperatures within the 18 x 14kg assembly.

This figure clearly shows the thermal ignition sequence of each of the drums instrumented. Thermal ignition can be seen to commenced at the geometric centre of the stack formed by the containers located at position 1 and 4 and then progress to the surrounding containers.

Figure 7.3.6 shows the temperature time history of the drums located at positions 1 and 4 in figure 7.3.2. The local air temperatures surrounding these drums when heated at an ambient temperature of  $57.0^{\circ}\text{C} \pm 0.4^{\circ}\text{C}$  is also included.

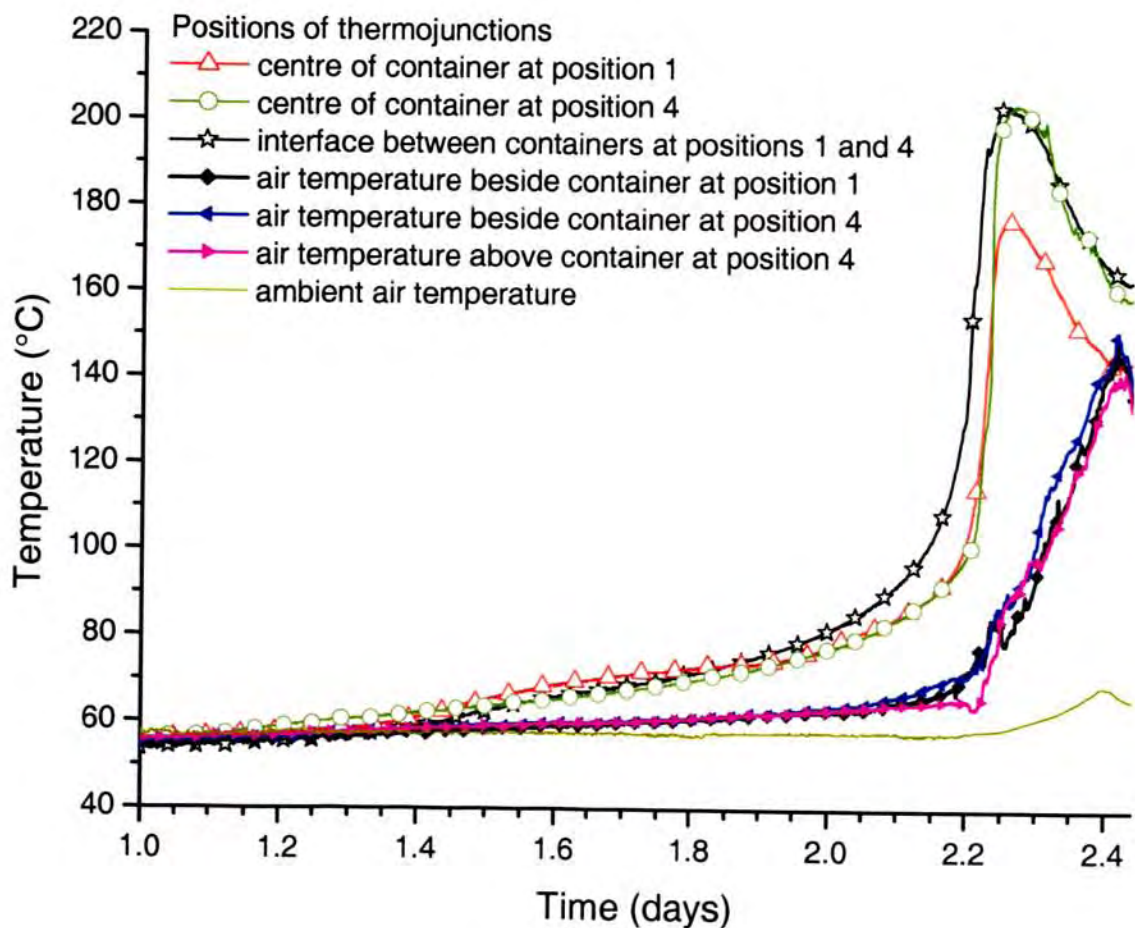


Figure 7.3.6: Super-critical temperature profile of the containers located at position 1 and 4 and the air temperatures within the 18 x 14kg assembly.

The usual temperature rise as a result of thermal ignition is displayed, however, notice that the common air temperature within the box has risen above ambient oven temperature after 1.4 days and that the common air temperature has rapidly increased after the initial thermal explosion event. The data are shown again in figure 7.3.7 from 2.15 to 2.35 days.



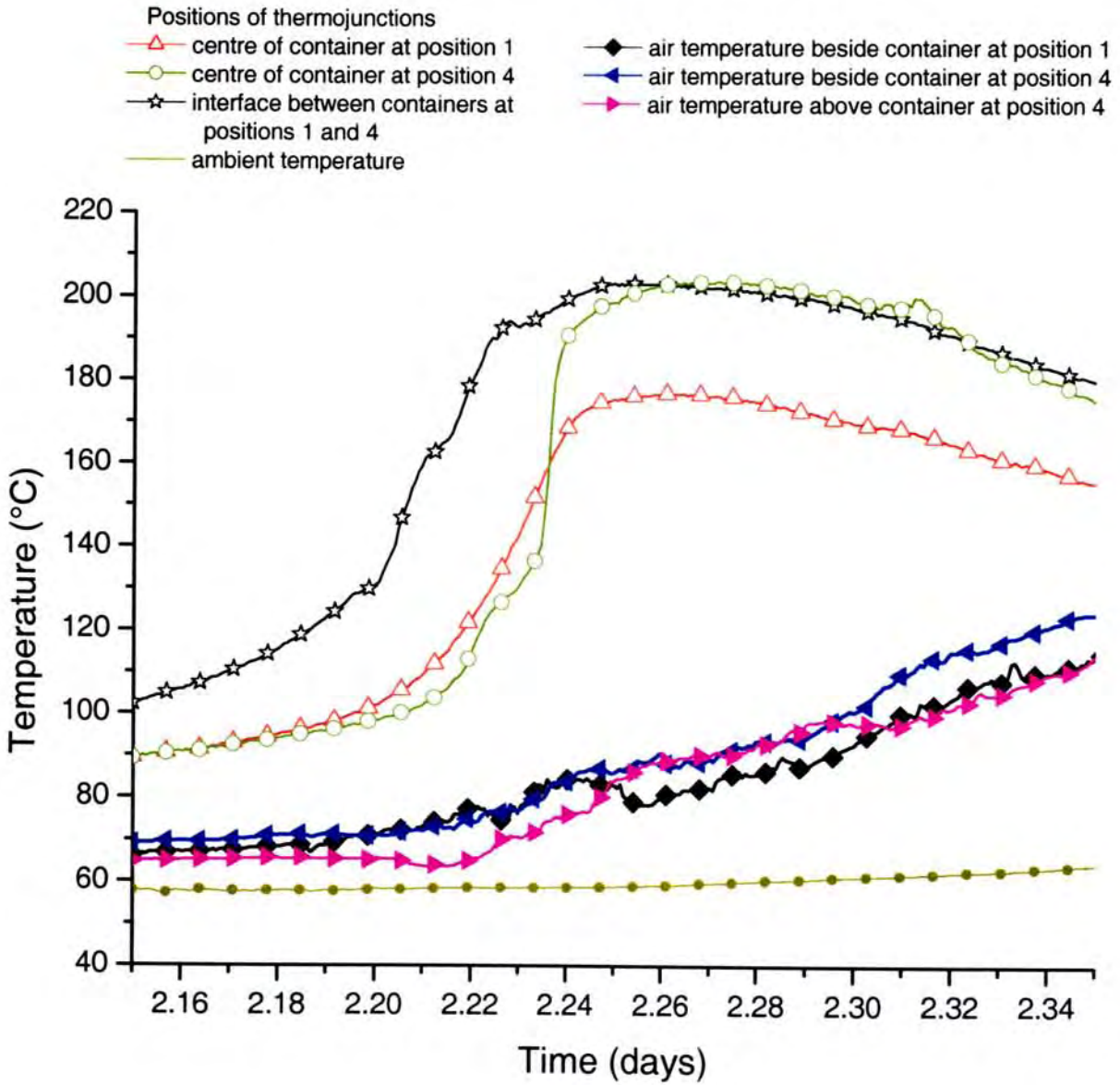


Figure 7.3.7: Temperature profile of the containers located at position 1 and 4 and the air temperatures within the 18 x 14kg assembly from 2.15 to 2.34 days.

Figure 7.3.7 clearly shows that thermal ignition commenced near the interface between the containers located at positions 1 and 4. Furthermore, this initial thermal ignition preceded the thermal ignition at the centre of containers these two containers by 20 minutes. Notice also, that the thermojunctions within the containers located at positions 1 and 4 and the thermojunctions in the air beside the containers located at positions 1 and 4, respond to the initial thermal ignition nearly simultaneously

after approximately 2.2 days. This is an expected result, since the distance from the position of the initial thermal ignition to the thermojunctions positioned within containers located at positions 1 or 4 is approximately the same as the maximum radius. These data suggest that thermal ignition commenced at the centre of the two containers at positions 1 and 4, producing a spherical thermal front radiating outwards at a velocity of approximately 6mm/minute. The front reached the HDPE edge at roughly the same time as it passed through the positions of the thermojunctions located within containers located at positions 1 and 4, resulting in the thermal ignition of the hydrated HCH at these positions. Notice, however, the relatively small differences in heating rates between the thermojunction located beside the container located at position 4 and container 1 up until day 2.2, after day 2.2. This increased rate of temperature rise of the thermojunction located at the centre of the container located at position 1 suggests that the origin of the thermal ignition is closer to the centre of the drum located at position 1 than the drum at position 4.

The mechanism by which the steel box lowered the CAT of the assembly compared to that of the single container, is explicitly shown by the above data. From approximately 5 hours after the assembly reached ambient temperature, the heat generated by the self-heating sample exceeded the heat leaving the ensemble, resulting in the progressive increase in local air temperatures above that of the oven. The above data also show that at approximately 30 minutes before the first thermal ignition event, the local common air temperature surrounding the container located at position 1 was 11°C higher than the ambient oven temperature, while the air surrounding the container located at position 4 was 14°C greater than the ambient oven temperature. Furthermore, given that the thermal lag time of the centre of these containers to an external temperature change is approximately 30 minutes, then these local air temperatures are well above the CAT of a single HDPE container.

The above data also show that complex convective motion develops within the common airspace. The data suggest that up to a time of approximately 1.9 days, the air within the box heats with little convection. This would be expected as the box is suspended within an isothermal air bath. Spatial



temperature stratification is evident, however, there is little suggestion of convective mixing since the three air temperature traces show a relatively linear temperature rise. Also, notice that over the period between day 1.5 and 2.2, the maximum temperature is not at the top of the container located at position 4, as one might expect for a convective system, but rather beside this container. This suggests that a near static layer of air exists above the container located at position 4, with this layer cooled by its close proximity to the steel surface of the box. Conversely, if this were not the case and significant convective motion was present within the air space contained by the steel box then it would be expected that the greatest temperature would occur in the upper air space of the box. Notice that between day 2.0 and day 2.2 the air temperature above the container at position 4 initially reduces by approximately 2°C before increasing in temperature. This is an important feature and provides further evidence of a transition to a different heat transfer regime over this time period; suggesting that the static air between the top of the container and the steel surface has been disrupted presumably by the onset of convection. Notice also, that this initial temperature reduction quickly reverses as additional heat enters the airspace from the decomposing HCH. The complex convective behaviour is also clearly displayed by the transient nature of the temperature trace of the thermojunction located within the airspace beside the container located at position 1.

Figure 7.3.8 includes the fate of the middle two containers as well as four instrumented containers located in the other geometrically different positions within the assembly.

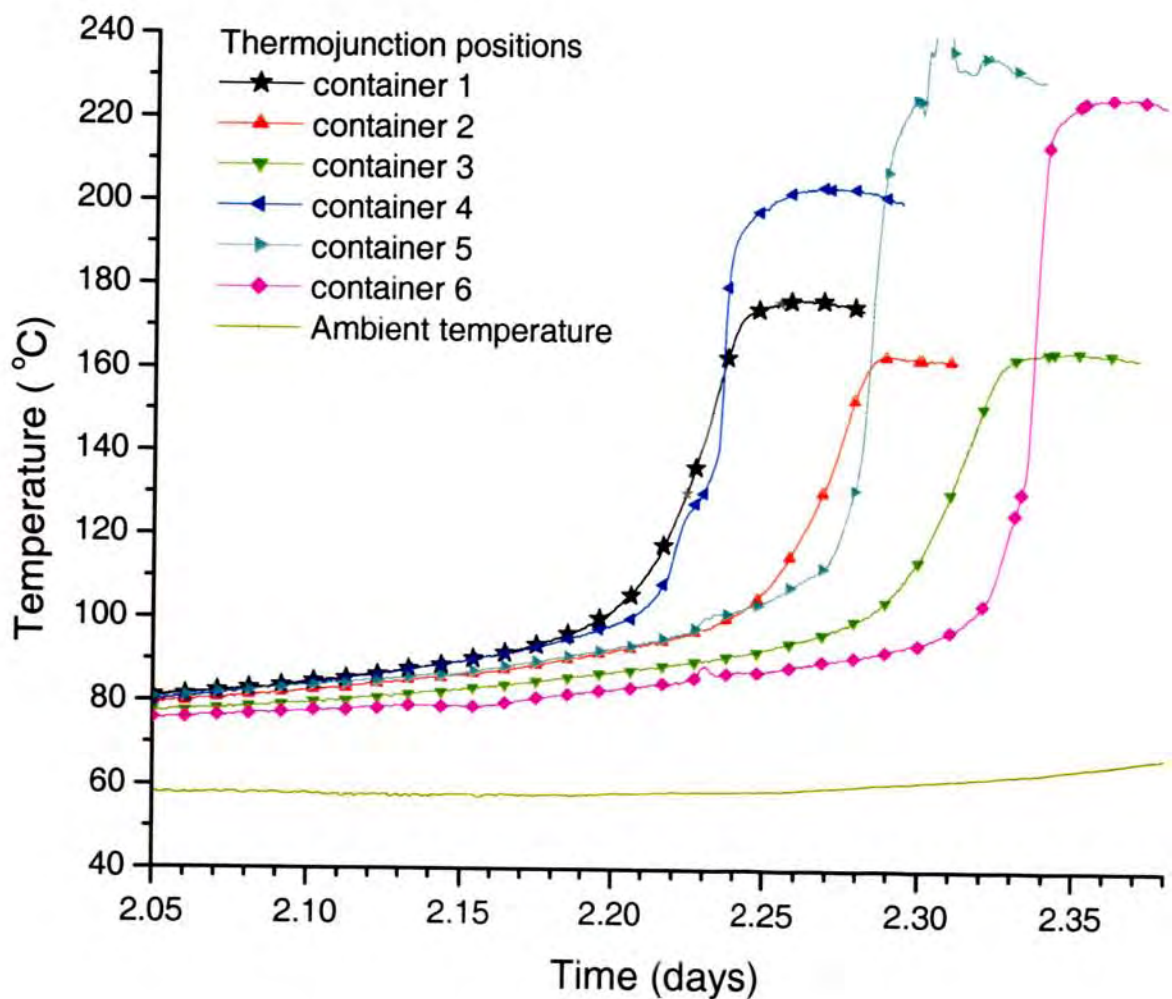
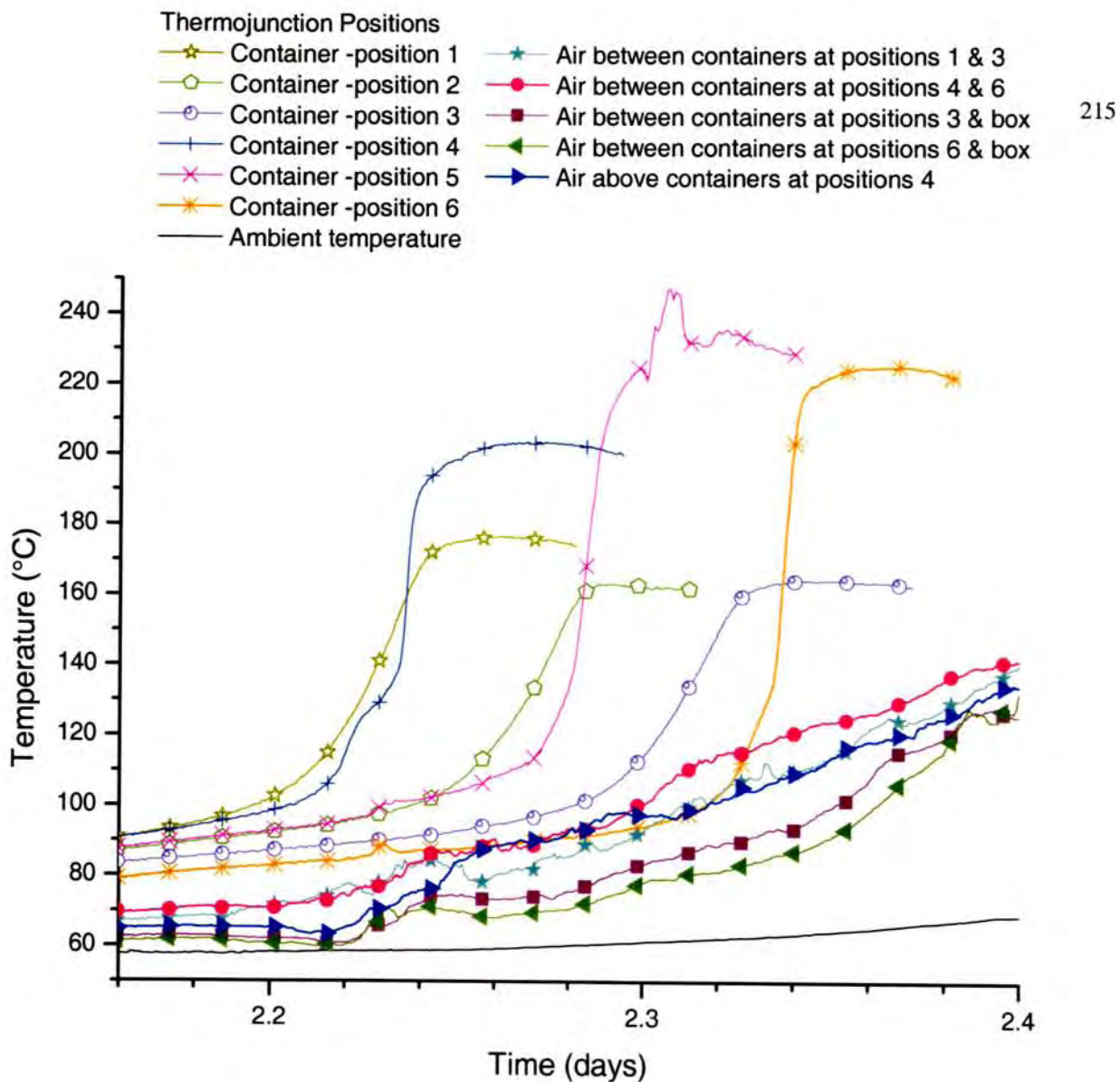


Figure 7.3.8: Super-critical temperature profile of all instrumented containers within the 18 x 14kg assembly.

Notice that a period of 45 minutes passes between the initial thermal ignition of containers at positions 1 and 4 and the thermal ignition of the containers located at positions 2 and 5, with a further 60 minutes passing before the thermal runaway of containers located at positions 3 and 6.

Figure 7.3.9 dramatically show the mechanism whereby the thermal ignition of the containers located at positions 2,3,5 and 6 were delayed relative to containers 1 and 4. Only, the section of interest is shown in this figure.



*Figure 7.3.9: Super-critical temperature profile of all instrumented containers within the 18 x 14kg assembly.*

Figure 7.3.9 shows that the position of maximum air temperature remained close to the geometric centre of the box until the onset of convection. This can be seen by the air temperature traces of the thermojunctions located beside the containers located at positions 1 and 4. Notice that the air temperature beside to the containers located at position 1 and 4 remains hotter than the air temperature between the containers located at position 3 and 6 and the steel wall, reaching a maximum difference of the order of 30°C at 2.34 days. The progressive increase in the common airspace temperature as each container undergoes thermal ignition is also clearly shown. This is most evident in the local air

temperature surrounding the containers located at the corners (positions 5 and 6) where the average local air temperature 30 minutes prior to thermal ignition of these containers is of the order of 85 °C . It is an interesting exercise to hypothesise the behaviour of this type of assembly if a further ring of containers were present. Consider an assembly of 50 containers stacked in two layers of 25 containers packed in rows of five. Also, assume similar times to ignition to those displayed by current experiment, that is 0.06 days for the containers located on the exterior face and 0.12 days for the corner containers. By extrapolation of the current air temperature data to 2.4 days it can be seen the perimeter containers in this larger configuration may be exposed to average air temperatures in excess of 120 °C 30 minutes prior to thermal ignition. Clearly, these data provide insight into the ignition pattern of HCH drums within a 6m shipping container.

The above figure suggests that a complex heating process occurs within the steel box with significant changes in the spatial temperature distribution developing throughout the experiment. The geometry of the assembly is such, however, that one could postulate that a degree of isolation would exist between the air movement of the inner air volume surrounding the containers located at positions 1 and 4 and the outer air layer between the box and containers located at positions 2, 3, 5 and 6, especially before the onset of convection. Furthermore, it might also be postulated that the resulting convection currents would circulate up through the centre air columns between the containers located at positions 1 and 3 and the containers located at positions 4 and 6 and down the cooler surface of the steel box.

The complete results for the measurement completed  $53.4^{\circ}\text{C} \pm 0.4^{\circ}\text{C}$  is shown in figure 7.3.10 and figure 7.3.11.



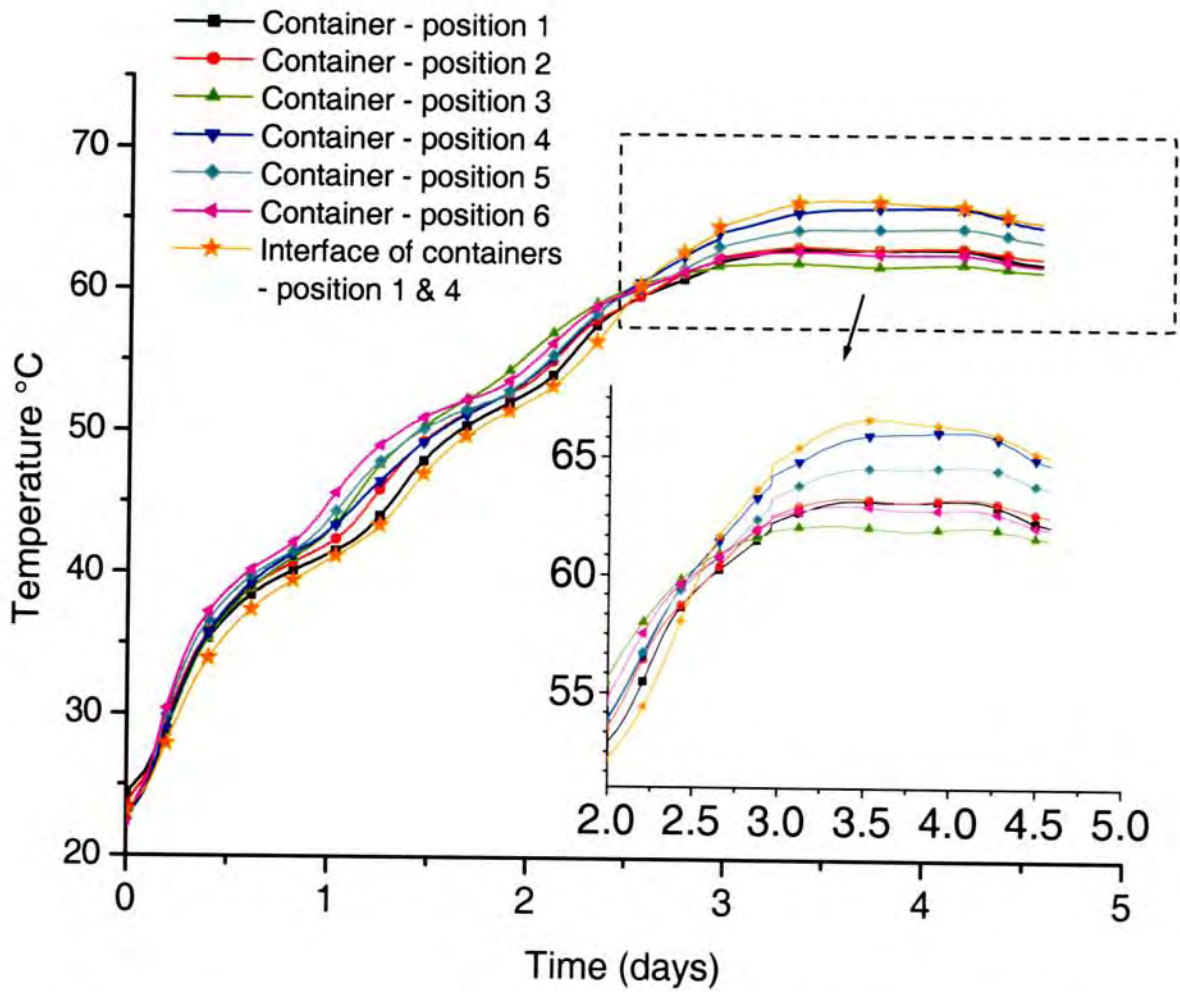


Figure 7.3.10: Sub-critical temperature profile of instrumented drums within the 18 x 14kg assembly

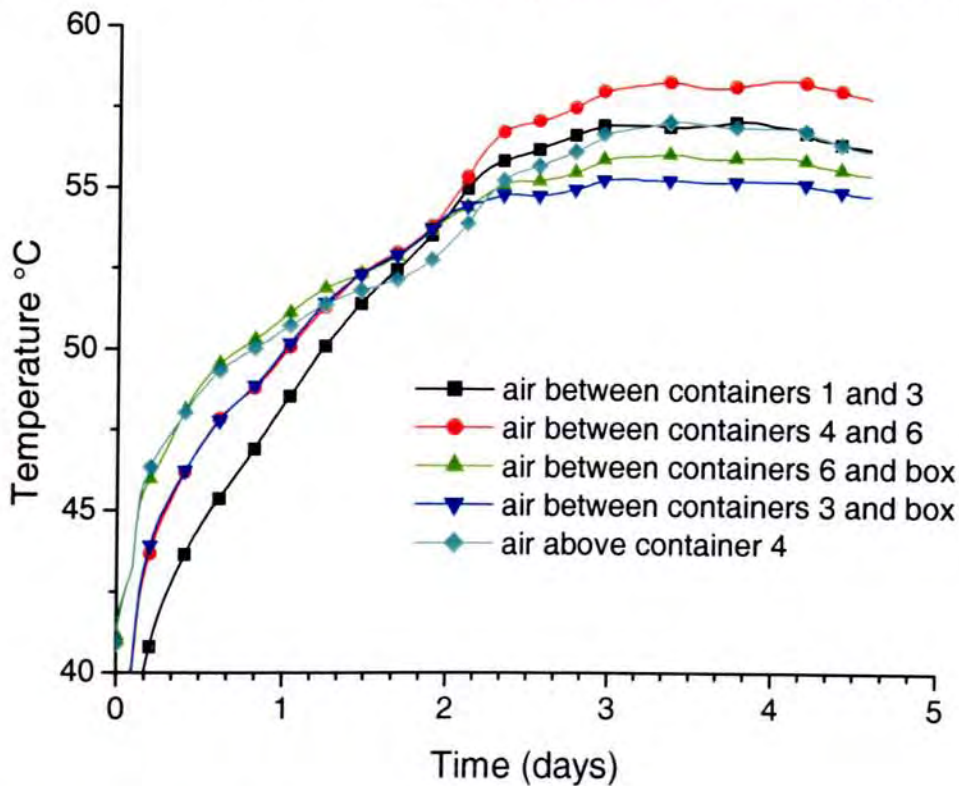


Figure 7.3.11: Sub-critical air temperature profile within the 18 x 14kg assembly

Figures 7.3.10. and 7.3.11. show similar heating features to the super-critical measurement. Thermal stratification in common air temperatures is again evident and notice that the interface between the containers located at positions 1 and 4 is again has the highest temperature. Clearly these data show that even with a moderate degree of self-heating the individual drums can ‘feel’ the heat flux from neighbouring drums.

#### **7.4. Investigation of the thermal ignition behaviour of stacked 40kg HDPE drums of hydrated HCH using conditions of natural convection**

The study described in section 7.3 suggested that the thermal ignition of a vertical stack two fully filled 14kg HDPE drums of hydrated HCH would commence at the geometric center of the stack. This geometry, however, differs from configuration where commercial drums of hydrated HCH are stacked, since an airspace will exist between each drum layer. While a similar amount of interactive heating would be expected for both configurations, the question must be asked as impact of the trapped airspace upon thermal ignition behaviour and the thermal ignition sequence of the drums. Hence, to examine the behaviour of stacked commercial drums of hydrated HCH the experiment discussed in this section was undertaken.

In this experiment two 40kg HDPE drums of hydrated HCH were stacked vertically within a steel box with a wooden floor with dimensions 0.612m x 0.612m x 0.952m. The apparatus described in section 5.3.3 and used in section 7.3.1 was used and the drums were instrumented in the standard way. Due to a limited quantity of sample, only a single experimental measurement was possible. As such, it was decided to complete the experiment a few degrees above the critical temperature for this drum size and hence, to qualitatively examine the general thermal ignition behaviour and compare the thermal ignition order to that displayed in section 7.3. Therefore, the CAT of this assembly was not ‘bracketed’. Figure 7.4.1 shows the results of this experiment.

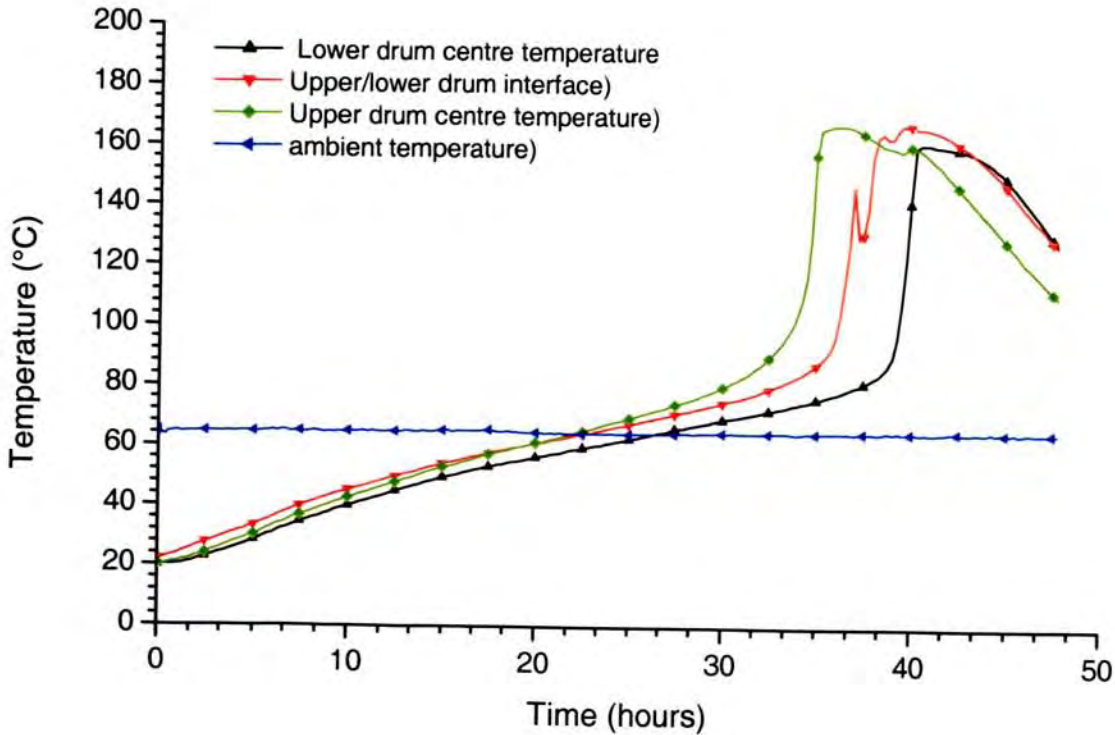


Figure 7.4.1: Super-critical behaviour of an assembly of two vertically stacked commercial, 40kg HDPE drums of hydrated HCH.

Qualitatively, the behaviour shown in figure 7.3.1 differs from the behaviour of the drums shown in figures 7.3.5 and 7.3.6. While the center stack of drums in figure 7.3.5 and 7.3.6 ignited from the geometric center, this is not the case when two commercial drums are similarly stacked. Notice in figure 7.4.1 that the thermal ignition commenced at the upper drum. Notice also that the thermal ignition times at the interface and at the lower drum suggest that thermal ignition progressed from the upper drum to the lower drum. These data suggest that the thermal ignition of commercial drums of hydrated HCH will behave, at least until the HDPE melts, more like individual drums rather than a long rod as described in section 7.4. Also notice that the rapid temperature rise of the upper drum occurred approximately five hours before the lower drum, clearly suggesting that the air temperature within the box is non-uniform.

## 7.5. Comparison between the SADT and the CAT of an assembly of 18 x 14kg HDPE drums of hydrated HCH.

As an extension to the SADT test comparison discussed in section 6.7 a SADT test was completed to assess how reliably the SADT reflects the CAT of a shipping container loaded with many individual drums of hydrated HCH. It should be again noted that the SADT states that 'The sample must be in the packaged form intended for commercial use' (UN, 1975: 28.4.1.2.1). For this current simulation, it was assumed that the packaged form intended for commercial use was the individual container. In this case, a SADT was completed upon a 14kg HDPE drum of hydrated HCH that had been prepared in an identical manner to all the other drums in this chapter. Figure 7.5.1 shown the result of this comparison.

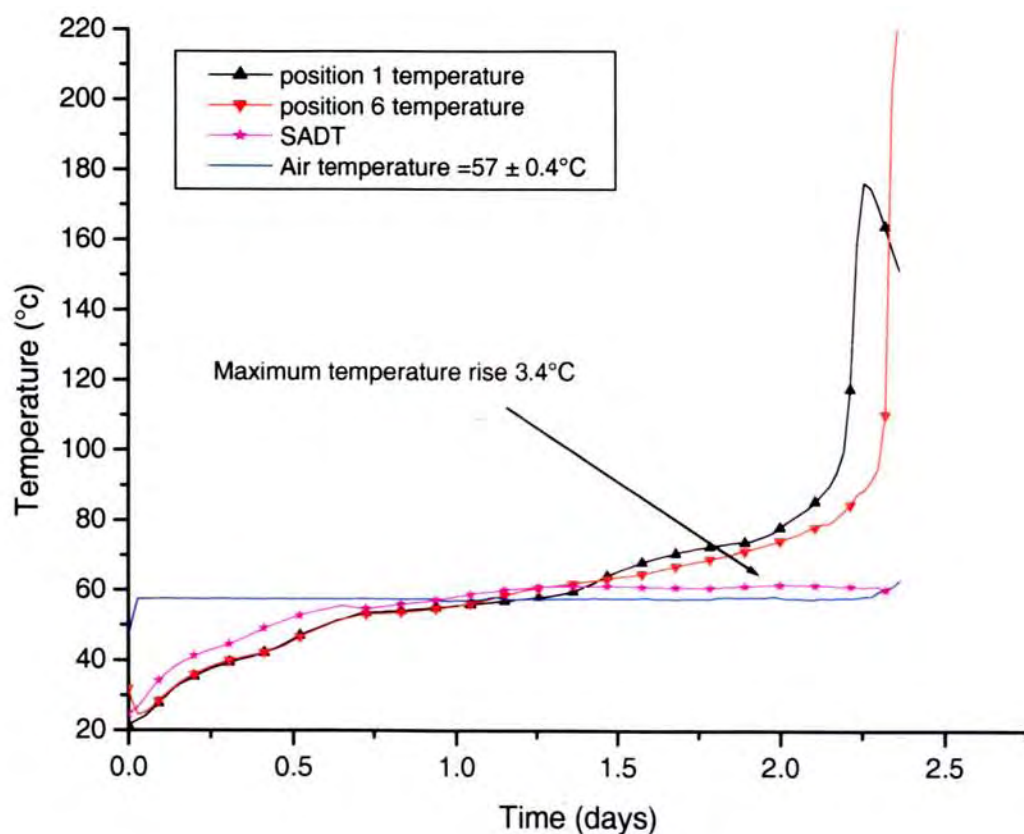


Figure 7.5.1: Comparison between the SADT of a 14kg drum of hydrated HCH and the CAT of the assembly measure in the previous section.



The unreliability of the SADT test for determining the critical ignition temperature of an assembly of self-heating bodies is self-evident in the above figure. In the above example, the SADT would have reported that the sample was allegedly safe to transport at this temperature. Clearly, the definition used to define the test package presents a significant safety problem for the maritime industry.

**7.6. Heat transfer coefficient measurement of shipping container**

To predict accurately the CAT of a shipping container packed with hydrated HCH, in addition to accurate kinetic and thermodynamic parameters, the heat transfer coefficient of the shipping container was also required. The apparatus and method discussed in section 7.6 was used and the results of this are shown in tabular form in table 7.1 and graphical form in figure 7.6.1.

**Table 7.1**  
**Temperature rise and electrical Power results from heat transfer coefficient measurements of a 6 m shipping container.**

Temperature rise ( $\Delta T^{\circ}\text{C}$ )	Power (W)
7.9	1867
18.85	4957
19.4	5106
25.4	6666
32.4	8929

These results tabulated in table 7.1 are plotted below assuming Newton’s law of cooling enabling the heat transfer coefficient to be calculated from the slope of the line.

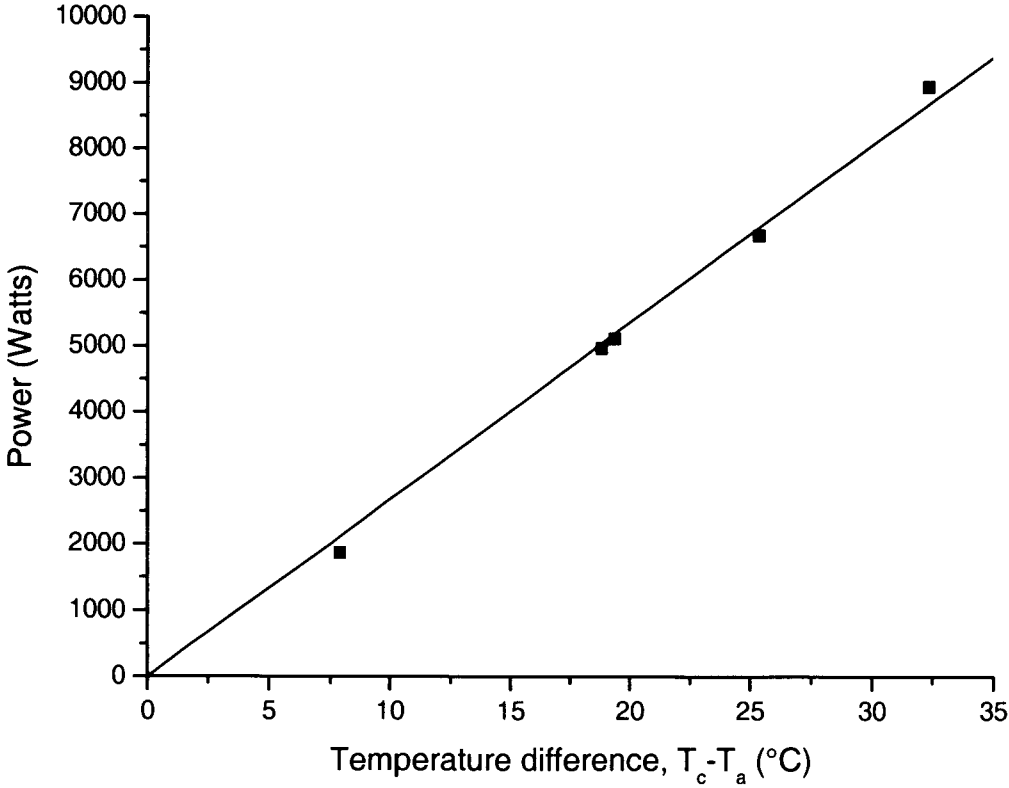


Figure 7.6.1: Plot of the power and temperature data for the determination of the heat transfer coefficient of a shipping container.

From the gradient of the plot above figure, the heat coefficient for the freight containers was determined to be  $3.5 \text{ W/m}^2\text{K}$

## 7.7. Interpretation

The results of the CAT study undertaken in this chapter are shown in table 7.1.

**Table 7.2**

Measurement	Critical Ambient Temperature (°C)
Single 14kg drum in forced convection (SADT conditions)	62.5 ± 2
18 x 14kg drums packed into a steel box (Still air conditions)	55 ± 2

Using the formula developed by Gray (2000) and presented in 1.2.4.2, the CAT values for the assembly of drums investigated in this chapter can be calculated. The measured CAT's as well as the calculated CAT's of freight container quantities of this material are shown in table 7.2

**Table 7.3**

Determination	Measured CAT (°C)	Calculated CAT (°C)
18 x 14kg drums packed into a steel box	55 ± 2	56.2
432 x 40kg HDPE packed in a freight container		42.6
80 x 200kg fibre packed in a freight container		31

The above table shows good correlation between the measured and calculated CAT for the assembly studied in this current chapter.

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It should be again noted that the model calculates CAT values using the assumption of 'well stirred' air conditions within common airspace. As discussed in section 1.2.3, while this assumption simplifies the solution of underlying formula, it does not significantly impact upon the calculated CAT value of the assembly. By examining the sensitivity of the calculated CAT to the heat transfer coefficient through the common airspace, it is found that the calculated CAT is upper bounded as the heat transfer coefficient tends to infinity. The upper bound for 432 x 40 kg drums of hydrated HCH is 44.6°C while the upper bound for 80 x 200kg drums is 32.5°C. Hence, the CAT values calculated using the well-stirred assumption tend to be closer towards this upper limit and are thus less conservative. Given that the calculated CAT values tend to reduce as the well stirred assumption is removed, combined with the calculated CAT values in the second two rows in table 7.2, very significant concerns exist regarding the safety of transporting large quantities of this material.

The behaviour of the air inside the box during both the sub-critical and super-critical interaction experiments gives very useful information regarding the mechanism by which the heat balance is modified as a result of the additional thermal resistance of the steel box (or freight container). The accumulation of heat within the common air environment was found for each interaction experiment resulting in an increase in the local air temperature surrounding each drum. While the detail of this behaviour has been discussed previously, this information forms further strong evidence to vindicate the model proposed by Gray (2000).

## 7.8. Discussion

The results of this current study have shown that the idea of interactive heating as proposed by Gray (2000), is essentially correct. Even with only 18 drums packed within a confined space, a significant lowering in CAT was found compared to a single drum. Other than the experimental determination of the CAT of a full sized freight container of this material, the CAT values using this model represent the most reliable available, for the given assumptions of the model.

The results of this study also suggest that the CAT of a closed drum of hydrated HCH, such as the commercial drums used in this study, are sensitive to the degree of filling. These current results suggest that the completely filled drum may possess a slightly lower CAT than a drum that possesses an airspace above the reactive sample. While this aspect has not been investigated fully in this current study, this finding has potential implications for both the manufacturing and transport industries of this material, if the percentage loading of commercial drums was increased. This aspect may have implications with respect to the reproducibility of the industrial filling process of each drum.

The data from this study has alluded to the thermal ignition sequence of the individual hydrated HCH. The data suggest that thermal ignition would commence in the centre of the loaded freight container and progress sequentially outwards. The outermost individual drums, while the last to ignite, would also experience the greatest local air temperatures that have been shown to be at least 100°C above the temperature outside the freight container, but could possibly be several hundreds of degrees above this exterior temperature. It is possible with such a rapid rise to such extreme temperatures that explosions may be induced, commencing in the outer layers of this assembly; this is especially the case when transported in closed steel drums.

The results of this study have general implications for any industry that wraps or transports drums or packages of self-heating material. The innocuous 'shrink wrapping' of pallets could, under certain

conditions reproduce the general findings of this current study. If the relative magnitudes of the heat transfer coefficient through the film to the convective heat transfer at the film/air interface is considered, then the overall heat transfer coefficient is significantly influenced by the latter. As such, the overall heat transfer coefficient value is insensitive to the type of material enveloping the stacked drums. Thus, when an assembly of the self-heating bodies is shrink wrapped onto a pallet, the overall CAT will be lower than that of the individual unit. Clearly, this effect has significant implications where the reactive material is shrink wrapped onto a pallet and then packed into a freight container or onto an enclosed truck.

If the SADT test is again examined, then an additional shortcoming, to those already discussed in chapter 6 becomes apparent in the definition of the term 'package'. Given the vagueness of this definition (discussed in section 6.10), the test not only does not account for the prevailing convective conditions surrounding individual drums, but it also fails to specifically address the interactive heating issue. In this aspect, the definition of the term 'package' clearly becomes most important. If the test is undertaken on the largest individual drum (not the complete assembly) then the SADT measured would clearly NOT reflect the actual critical ignition temperature of the freight container. In this case, the maximum 'safe' temperature reported for transportation could be many degrees above the critical ignition temperature of the assembly. It is important, therefore, in situations where the freight container itself has the potential to lower the overall critical ignition temperature of a complete assembly, to undertake this test on a loaded freight container. The conundrum for this scale test to be meaningful, however, is that the arbitrary time limit would need to be removed, since a body of this size would most likely display an induction period that would exceed of the 7 day time limit.

A further interesting aspect to this self-heating problem becomes evident when the time to ignition of the loaded freight container is also considered. From a self-heating perspective only, consider the situation where very massive individual drums are packaged into a freight container. In this case, the induction time of the body would exceed the typical voyage period of approximately 1-2 months. The

freight container, in this case, would be unpacked well before the temperature of the individual drums reached the ambient hull temperature aboard the ship. Hence, while this size assembly would be classified as very super-critical, it could be safely transported as long as the voyage time was not greatly extended. Indeed, many reactive substances are transported in this manner including coal and live animals, where the coal or feed stored in the hold is generally of a super-critical size. If the individual drums size considered is now progressively reduced, then the assembly, as a result of the reduced induction time and corresponding increased in critical ignition temperature, could reach an optimal size whereby thermal runaway would be possible during a typical voyage. Clearly, this would depend upon the relationship between the critical ignition temperature and the induction time of the body. At the other extreme, for individual drum that are smaller than this optimal size, the critical ignition temperature would be so high that this temperature would not be achieved during normal voyages. Hence, for a given transport time and hull temperature, a critical size/s may exist which are of optimal size for thermal ignition. An interesting aspect here is that from a self-heating perspective only, it would be safer to transport very massive individual packages, a point that would seem, upon first consideration, to contradict the usual thinking regarding size and safety of self-heating bodies.

## 7.9. Conclusions

- 1 The predictions of the theory of interactive heating proposed by Gray (2000) that addresses the concept that heat generating bodies when placed in close proximity within a finite capacity heat bath, interact to lower the overall critical ignition temperature of entire ensemble, is in accordance with the experimental results of this current study.
- 2 The CAT of 18 x 14kg HDPE drums of hydrated HCH, when packed into a close fitting steel box, is 7°C lower than the CAT for a single identical drum placed in the identical heating environment

- 3 The SADT test is not capable of addressing the interactive heating affects that occur when many self-heating bodied are closely packed within a larger container of finite heat capacity.
- 4 The SADT test has significant potential to report an unreliable 'safe' transport temperature that, under certain conditions, may be many degrees larger than the critical ignition temperature of the body.
- 5 The induction period of an assembly of self-heating bodies is greatly increased as a result of the overall thermal resistance of the larger container.



## Chapter 8

### Conclusion

#### 8.1 Preamble

As stated in chapter 1, this thesis is concerned with the investigation of the self-heating phenomenology of bagasse and the spontaneous thermal ignition of calcium hypochlorite. While these materials are chemically and physically different they present related spontaneous combustion hazards for each respective industry. The emphasis of this thesis has been to provide experimental evidence from which predictions can be made regarding the spontaneous combustion hazard when industrial quantities of these materials are stored or transported. For both materials, the experimental approach has followed an initial laboratory scale investigation followed by large scale field measurements. In both cases, the experimental laboratory data as well as the field measurement have provided key data for a predictive mathematical model. This chapter presents the conclusions drawn from the results of each study.

#### 8.2 The self-heating of Bagasse.

Chapter 2 presents the findings of laboratory measurements from oxidation and isothermal calorimetry measurements on bagasse. This study found:

1. Bagasse exhibits a strong moisture dependence with respect to reaction rate at moistures of greater than 30% (dry basis). Negligible reaction is displayed at moisture contents below 25 to 30%, while at moistures above this value, oxidation rates of up to  $6 \text{ nmol g}^{-1} \text{ s}^{-1}$  of oxygen are displayed.
2. At temperatures of  $50^\circ\text{C}$  oxidation rates in the order of  $0.8 \text{ nmol/g/s}$  of oxygen have been measured while at  $60^\circ\text{C}$  oxidation rates between  $0.09$  and  $0.8 \text{ nmol/g/s}$  of oxygen have been measured. Peak oxidation rates of  $3.1 \text{ nmol/g/s}$  of oxygen and  $6.9 \text{ nmol/g/s}$  of oxygen have been measured at  $70^\circ\text{C}$  and  $90^\circ\text{C}$  respectively.
3. The rate of heat generation from bagasse has been measured to be directly related to the rate of oxygen consumption.

4 The oxidation chemistry of bagasse is complex with samples from different seasons displaying significantly different oxidation and heating behaviour. Bagasse from the 1997 season displayed reduced reactivity compared to the sample from the 1996. It is not known whether this difference is due to seasonal or regional factors as the exact source of the bagasse is unknown.

Chapter 3 presents the results of large scale field measurements upon bagasse stockpiles designed to simulate simple infinite slab type geometry. The temperature, moisture and permanent gas concentration was measured for stockpiles of different widths and densities.

These measurements found that:

1. Bagasse stockpiles of sufficient width, can quickly self-heat to a quasi-steady-state temperature following formation. While at this temperature, the stockpile loses moisture by evaporation and diffusion processes until the moisture concentration falls below a critical concentration, whereby the heat release rate drops significantly and the stockpile cools to a temperature close to ambient air temperature.
2. Following cooling from the quasi-steady-state temperature, the bagasse stockpile will remain stable with little heat being produced.
3. After cooling from the quasi-steady-state temperature, a stable bagasse stockpile may undergo further wet oxidation with an associated rapid thermal increase if the stockpile is sufficiently remoistened.
4. The Reaction-diffusion model of Stored Bagasse (Macaskill, Sexton and Gray, 1998) captured the main self-heating features of the experimental results discussed in that chapter.

5. It is possible, using the energy generated by the wet oxidation reaction, to dry bagasse from its nominal moisture concentration of 50% (wet basis) to a minimum moisture concentration of between 15 and 25%. This aspect may have industrial applications if a cost effective storage method can be developed.

As a conclusion the, results of the investigations into the self-heating of bagasse suggest that the self-heating of bagasse (and cellulosic materials in general) is not a result of microbial action as has been suggested by other researchers Rothbaum (1963). This is clearly an area for further work.

### **8.3 The self-heating of Hydrated Calcium Hypochlorite**

Chapter 6 presents the results of CAT measurements of up to 200kg on commercial hydrated calcium hypochlorite. These measurements found that:

1. The thermal decomposition of hydrated HCH involves at least two distinct reactions. Each reaction is individually consistent with F-K theory of thermal ignition over a limited temperature range.
2. The activation energy of the reaction that is dominant below 120°C is  $48.5 \pm 1.8 \text{ kJ mol}^{-1}$
3. Biot numbers for commercial containers of hydrated HCH are in the region where the critical ignition temperature is sensitive to the surrounding heat transfer characteristics.
4. Correction for finite Biot number has improved the agreement of the raw experimental data to F-K theory.
5. The CAT of a 40kg container, measured using forced convection conditions in a temperature controlled oven, is 60.1°C while the CAT of an identical container, measured using conditions of natural convection, is 55.2°C
6. The CAT of a 200kg drum, measured using conditions of natural convection, is 43.4°C.

7. The use of small-scale, and therefore high temperature data alone for the prediction of the critical ignition temperature for commercial quantities of hydrated HCH, will give incorrect values that may be up to 40°C above the CIT.
8. The SADT test has the potential to report an unreliable and more importantly, report a less conservative; 'safe' transport temperature for a material with a low Biot number.
9. The results of the measurements in chapter 6, combined with the calculated low activation energy, suggest that the critical ignition temperature of commercially shipped quantities (13 – 18 tonnes) of hydrated HCH may be in the temperature range prevailing within the holds of ships, particularly in tropical waters.
10. At the time of thermal runaway, HCH can produce sufficient temperature rise to ignite the HDPE containers that are commercially used to transport this material.

Chapter 7 presents the results of experiments on the interaction effect exhibited when a number of drums undergoing self-heating are placed within a confined space. The findings of this study were:

- 1 The predictions of the theory of interactive heating proposed by Gray (2000) that addresses the concept that heat generating bodies when placed in close proximity within a finite capacity heat bath, interact to lower the overall critical ignition temperature of entire ensemble, is in accordance with the experimental results of this current study.
- 2 The CAT of 18 x 14kg HDPE drums of hydrated HCH, when packed into a close fitting steel box, is 7°C lower than the CAT for a single identical drum placed in the identical heating environment
- 3 The SADT test is not capable of addressing the interactive heating affects that occur when many self-heating bodied are closely packed within a larger container of finite heat capacity.
- 4 The SADT test has significant potential to report an unreliable 'safe' transport temperature that, under certain conditions, may be many degrees larger than the critical ignition temperature of the body.

- 5      The induction period of an assembly of self-heating bodies is greatly increased as a result of the overall thermal resistance of the larger container.

In both of the investigations presented in this thesis the results obtained have been used to address industrial spontaneous combustion hazards. The bagasse study has provided key data for the model by Macaskill, Sexton and Gray (1998). This model is currently used as a predictive tool to evaluate the spontaneous combustion hazards of bagasse stockpiles of various sizes and geometries. The calcium hypochlorite study has similarly provided key experimental data. The model of Gray (2000) has been used as a predictive tool to determine the critical ignition condition for commonly transported quantities of calcium hypochlorite.

# BIBLIOGRAPHY

- Abraham, C.J., (1996) A solution to spontaneous combustion in linseed oil formulations *Polymer Degradation and Stability*: 54: 157-166.
- Adler, J.,(1983) Thermal Explosion Theory for a Slab with Partial Insulation *Combustion and Flame*: 50: 1-7.
- Allardice, D.J., (1991) The Water in Brown Coal, in Durie, RA., *The Science of Victorian Brown Coal*, Butterworth-Heinemann Ltd, Oxford:104-151.
- Allardice, D.J. And Evans, DG., (1971) The-brown coal/water system: Part 2. Water sorption isotherms on bed-moist Yallourn brown coal, *Fuel*, 50: 236-253.
- Allardice, D.J., (1968) *The Water in Brown Coal*, PhD thesis, The University of Melbourne.
- American Standard Test Methods., (1995) Standard Test Methods of Sampling and Chemical Analysis of Chlorine-Containing Bleaches, *Designation: D 2022 –89(Reapproved 1995)*: 1-8.
- Ashbolt, N.J., (1986) Bagasse Storage Microbiology, Annual Technical Conference, Sugar Research Institute, Mackay, QLD, August 1986 (Internal Report).
- Ashbolt, N.J., (1985) Deterioration of bagasse during storage, Annual Technical Conference, Sugar Research Institute, Mackay, QLD, August 1985 (Internal Report).
- Atkins. P.W., (1982) *Physical Chemistry*, Oxford University Press, Oxford.
- Barzykin, V.V., Gontkovkaya, V.T., and Merzhznov, A.G., (1966) Theory of thermal explosion of self-accelerating reactions, *Fizika Goreniya I Vzryva* 2, 4: 18-23.
- Bennet, C.O. and Myers, J.E.,(1962) *Momentum, Heat and Mass Transfer* McGraw-Hill Book Company Inc, New York.
- Bibby, D.M. and Milestone, N.B., (1984) The Decomposition of High Grade Bleaching Powder (Calcium Hypochlorite) *Journal of Chemistry, Technology and Biotechnology*: 34A: 423 – 430.
- Boddington, T., Fenng, C.G. and Scott, S.K. (1984) Thermal Explosion of dispersed media: criticality for discrete reactive particles in an inert matrix, *Journal of the Chemical Society, Faraday Transactions 2*: 90 973-983
- Boddington, T., Feng, C.G. and Gray, P., (1983) Thermal Explosions, Criticality and Transition in Systems with Variable Thermal Conductivity Distributed Temperatures *Journal of the Chemical Society, Faraday*: 2, 79: 1499-1513.
- Boddington, T., Griffiths, J.F. Scott, S.K. and Hansson, J., (1982) Thermal Explosion of dispersed media: criticality for discrete reactive particles in an inert matrix, *Proceedings of the 6<sup>th</sup> Symposium of the Stability of Explosives*: 129
- Boddington, T., Gray, P. and Robinson, C., (1979) Thermal explosions and the disappearance of criticality at small activation energies: exact results for the slab *Proceedings of the Royal Society of London*: A 368: 441-461.
- Boddington, T., Gray, P. and Harvey, D.I.,(1971) Thermal theory of spontaneous ignition: criticality in bodies of arbitrary shape *Proceedings of the Royal Society of London*: 270, A 1207: 467-497.

- Bowes, P.C., (1984) *Self-heating: Evaluating and controlling the hazards* Elsevier Science publishers B.V. Amsterdam.
- Bowes, P.C. and Thomas, P.H., (1966) Ignition and Extinction Phenomena Accompanying Oxygen-dependent Self-heating of Porous Bodies *Combustion and Flame*: 10: 221-230.
- Burgoyne, J.H., Gibson, N., Mann, R. and Palmer, R., (1981) *Runaway Reactions, Unstable Products and combustible Powders* The Institution of Chemical Engineers, Rugby.
- Calvet, E., (1948) A new differential microcalorimeter with electrical compensation *Academie Des Sciences*: 226: 1702-1704.
- Cane, R.F., (1983) Calcium hypochlorite- a hazardous substance *Fire Engineers Journal* June: 41-43.
- Cane, R.F., (1978) Calcium hypochlorite- a potentially hazardous product *Chemistry in Australia* 45, 9: 313-314.
- Cardillo, P., and Nebuloni, M., (1994) Reactivity and Thermal Stability of Calcium Hypochlorite, *La Rivista dei Combustibili* 48, 7-8: 300-305.
- Carras, J. N. 2000, Personal Communication.
- Carras, J. N. and Young, B. C. Self-Heating of Coal and Related Materials: Models, Application and Test Methods *Prog. Energy Combust. Sci.*, 1994, **20**, 1-15.
- Carslaw, H.S. and Jaegar, J.C., (1959) *Conduction of Heat in Solids* Clarendon Press, Oxford.
- Chambre, P.L. (1952) *Journal of Chemistry and Physics* 20: 1795.
- Clancey, V.J., (1975) Fire Hazards of Calcium Hypochlorite *Journal of Hazardous Materials*: 1: 83-94.
- Cocke, J.B., (1974) Effect of Seed-Cotton moisture Level at Harvest on Ginned Lint *Production Research Report No. 157*, Agricultural Research Service, United States Department of Agriculture.
- Dahn, C.J., (1979) Results of Hazards Tests of Calcium Hypochlorite. *Safety Consulting Engineers Inc. 5240 Pearl Street, Rosemount, Illinois 60018*. Final Report No 9281279.
- Davis, J.D. and Byron, J.F., (1924) An Adiabatic Method for studying Spontaneous Heating of Coal *American Ceramic Society Journal* 7: 809-816.
- Dawson, M.W., Dixon, T.F. and Inkerman, P.A., (1990) Moisture loss from Baled Bagasse during Storage *Proceedings of Australian Society of Sugar Cane Techologists*: 12: 199 – 206.
- deHann, J.D., (1996) Spontaneous Ignition, Part II: Investigation, *Fire and Arson Investigator* : 46, 4: 8-11.
- Dixon, T.F., (1988) Spontaneous combustion of bagasse stockpiles *Proceedings of Australian Society of Sugar Cane Techologists*: 10: 53 – 61.
- Dixon, T.F., 1997 Personal Communication
- Dixon, T.F., 2000 Personal Communication
- Donaldson, A.B. and Shouman, AR., (1979) The Frank-Kamenetskii Problem Revised. Part I. Boundary Conditions of First kind *Combustion and Flame*: 36: 217-232.
- Drysdale, D., (1985) *An Introduction to Fire Dynamics* John Wiley and Sons, Chichester.

- Dye, M.H., (1964) Self-Heating of Damp Wool : *New Zealand Journal of Science*: 7, 1: 87-146.
- Edelstein, S M., (1960) Origins of chlorine Bleaching in America : *American Dyestuff Reporter* : 49: 39-48.
- Elwell, D. and Pointon, A.J., (1972) *Classical Thermodynamics*: Penguin Books, Hammersmith.
- Frank-Kamenetskii, D.A., (1969) *Diffusion and Heat Transfer in Chemical Kinetics*, Plenum Press, London.
- Firth, J.B. and Stuckey, R.E., (1947) Spontaneous Combustion of Hay *Nature*: 159: 624-626.
- Fowler, A.C., (1997) *Mathematical Models in the Applied Sciences* Cambridge University Press, Cambridge.
- Gates, S.C. and Becker, J., (1989) *Laboratory Automation Using the IBM PC* Prentice-Hall Inc, New Jersey.
- Gill, W., Shouman, A.R. and Donaldson, A.B., (1981) The Frank-Kamenetskii Problem Revised. Part II: Boundary Conditions *Combustion and Flame*: 41: 99-105.
- Gray, B.F., (2002) Personal Communication.
- Gray, B.F. and Halliburton, B., (2000) The Thermal decomposition of hydrated calcium hypochlorite (UN 2880) *Fire Safety Journal*: 35: 223-239.
- Gray, B.F. and Holleyhead, R., (1999) The Submissions to the International Maritime Organization (IMO): A Review, 27 January 2000.
- Gray, B.F., Holleyhead, R., and Halliburton, B.W., (1999) Annex 1- A study of the thermal properties of hydrated calcium hypochlorite (UN2880) , a Submission to the International Maritime Organization (IMO).
- Gray, B.F., (2000) On the Critical Conditions for an Assembly Interacting Thermons *Journal of Australian Mathematical Society*.
- Gray, B.F., Sexton, M.J., Halliburton, B., Macaskill, C., (Accepted for publication 2001, published 2002) Wetting-induced ignition in cellulose materials *Fire Safety Journal*: 37: 465 - 479 .
- Gray, B.F. and Carras, J.N., (1995) A preliminary report on the low temperature wet decomposition of bagasse March Internal report – Sugar Research Institute, Mackay.
- Gray, B.F., McIntosh, A.C. and Wake, G.C., (1994) Ignition of combustible material in reference of a damp atmosphere *Physics Letters*: A191: 61 – 70.
- Gray, B.F., Griffiths, J.F. and Hasko, S.M., (1984) Spontaneous ignition hazards in stockpiles of cellulosic materials: criteria for safe storage *Journal of Chemistry, Technology and Biotechnology*: 34A: 453 – 463.
- Gray, B.F. and Jones, J.C., (1981) Brief Communications – Critical Conditions in Chemically Reacting Systems *Combustion and Flame*: 40: 331-332.
- Gray, P. and Scott, S.K., (1990) *Chemical Oscillations and Instabilities* Clarendon Press, Oxford.
- Gray, P., Griffiths, J.F., Hasko, S.M. and Lignola, P.G., (1981) Oscillatory ignitions and cool flames accompanying the non-isothermal oxidation of acetaldehyde in a well stirred, flow reactor *Proceedings of the Royal Society of London*: A374, 313-339.



- Gray, P. and Lee, P.R., (1967) Thermal Explosion Theory *Oxidation Combustion Review*, Ed. C.F.H. Tipper, Elsevier, Amsterdam,: 2: 21. 1
- Greenspan, L., (1977) *J.Res. National Bureau of Standards*, 81A,89: 1977.
- Griffiths, J.F., Hasko, S.M., and Tong, A.W., (1985) Thermal Ignition in Packed Particulate Solids: Critically under Conditions of Variable Biot Number *Combustion and Flame*: 59: 1-9.
- Hodges, D.J., and Acherjee, B., (1965) An Isothermal Micro-Calorimeter *Laboratory Practice* 14,7: 842-850.
- Hodges, D.J. and Hinsley, F.B., (1964) The Influence of Moisture on the Spontaneous Heating of Coal *The Mining Engineer*: 1: 211-224.
- Hofmann, A.W., (1861) Spontaneous Decomposition of Chlorine of Lime *American Journal of Pharmacy* 9, 3: 72.
- Hoffman, E. J., (1940) *Journal of Agricultural Resources*, 61, 241
- Holman, J.P., (1971) *Experimental Methods for Engineers* McGraw-Hill Book Company, New York.
- International Maritime Organization (1999a) Amendments to the IMDG Code, its annexes and supplements (EmS, MFAG), including Harmonization of the IMDG Code with UN Recommendations on the Transport of Dangerous Goods. Amendments to 7.1.1.15 of the reformed IMDG Code, 2 December 1999/ German Submission.
- International Maritime Organization (1999b) Amendments to the IMDG Code, its annexes and supplements (EmS, MFAG), including Harmonization of the IMDG Code with UN Recommendations on the Transport of Dangerous Goods. Amendment 30-00 to the IMDG Code, its Annexes and Supplements – Carriage of calcium hypochlorite 3 December 1999/ German Submission.
- International Maritime Organization (1999c) Amendments to the IMDG Code, its annexes and supplements (EmS, MFAG), including Harmonization of the IMDG Code with UN Recommendations on the Transport of Dangerous Goods. Carriage of calcium hypochlorite 5 December 1999/ Canadian Submission.
- Jones, J.C., (1999) Direct determination of the Biot number in oven heating tests *Journal of Fire Sciences* 17: 421-429.
- Jones, J.C., (1993) *Combustion Science- Principles and Practice* Millennium Books, Newtown.
- Jones, J.C., Ramahti, H., Fowler, D. and Vorasurayakarnt, J. and Bridges, RG., (1990) The Self-Heating and Thermal Ignition Propensity of Forest Floor Litter *Journal of Fire Sciences*: 8: 207-223.
- Jones, J.C. and Suresh, C.R., (1987) The Self-heating and ignition of vegetation debris *Fuel*: 67: 1208-1210.
- Kassoy, D.R. and Linan, A., (1978) The Influence of reactant consumption on the critical conditions for homogeneous thermal explosions *Quarterly Journal of Mechanically Applied Mathematics*., 31, 1: 100-112.
- Kordylewski, W. and Krajewski, Z., (1981) Thermal Ignition of Self-Heating Porous Slab *Combustion and Flame*: 41: 113-122.

Laszlo, S., Miklos, K., Gyula, M. and Judit, D.H.,(1993) A Biomassza kemiai hasznositasa II *Evfolyam. D. Szam:* 48: 371-375.

Little, S.G., (1991) M.Sc. Thesis, School of Chemistry, Macquarie University.

Long, S.C., Seavey, D.L, Switzenbaum, M.S and Bailey, N.O (1998) Chemical inhibitors for biosolids pellets to promote stability during transport and storage *Water Environment Research:* 70, 3: 261-267.

Macaskill, C., Sexton, M.J. and Gray, B.F., (1998) A Reaction-diffusion Model of Stored Bagasse *Report 98-33: 1-9*, School of Mathematics and Statistics, University of Sydney.

Mandell, H.C., (1971) A New Calcuim Hypochlorite and a Discriminatory Test, *Fire Technology* 7, 2: 157-161.

Mulcahy, M.F.R., (1973) *Gas Kinetics* Thomas Nelson Australia Ltd, Melbourne.

Musselmann, H. H., (1935) *Michigan Agricultural Experiment Station, Quarterly Bulletin.* 17, 175.

Newman, P.C. (1957) A method for the measurement of heat generation in powdered coal *British Journal of Applied Physics:* 8, 4: 162-167.

Nordon, P., Bainbridge, NW., Szemes, F. and Myers, C., (1985) A low temperature reaction calorimeter of the Calvet type for the measurement of the heat of oxidation of coal *Journal of Physics E: Scientific Instrumentation:* 18: 338-341.

Ott, E., Spurlin, H.M. and Grafflin, M.W., (1954) *Cellulose and Cellulose Derivatives*, Interscience Publishers, Inc., New York.

Rackham, H., (1961) *PLINY- Natural History Volume V – English Translation* William Heinemann, Cambridge.

Rothbaum, H.P., (1963) Spontaneous Combustion of Hay *Journal of Applied Chemistry:* 13: 291-302.

Standards Australia (1991) Standards Australia Wiring Rules AS3000 & AS3008, Sydney.

Schmitt, C.R., (1996) 'Pyrophoric Materials Handbook – Flammable Metals and Materials'

Schrodinger Dr of Olin Chemicals.,(1979) private communication to Dr V. J Clancy. see [Gray, B.F., Holleyhead, R., and Halliburton, B.W.,(2000)]

Sconce, J.S.,(1962) *Chlorine, its manufacture, properties and uses*. New York, Reinhold Pub. Corp

Shreve, R.N., Brink, J.A Jr., (1977) *Chemical Process Industries* McGraw-Hill International Book Company, Tokyo.

Shonhardt, J.A., (1984) Calorimeter design and the assessment of self-heating in coal *The Coal Journal:* 11: 79-85.

Shuman, A.R., Donaldson, A.B. and Tsao, H.Y., (1974) Exact Solution to the One-dimensional Stationary Energy Equation for a Self-Heating Slab *Combustion and Flame:* 23: 17-28.

Silva, M.A., Nebra, S.A., Machado Silva, M.J. and Sanchez, C.G., (1998) The Use of Biomass residues in the Brazillian Soluble Coffee Industry *Biomass and Bioenergy:* 14, 5/6: 457-467.

Sisson, R.A., (1991) *Spontaneous Combustion of Cotton Stored Under Industrial Conditions*. Master of Science thesis.Macquarie University, NSW. Australia.

- Sisson, R.A., Swift, A., Wake G.C., and Gray, B.F., (1993) The self-heating of damp cellulosic materials.II. On the steady states of the spatially distributed case *IMA Journal of Applied Mathematics* 50: 285-306.
- Sisson, R.A., Swift, A., Wake G.C., and Gray, B.F., (1992) The self-heating of damp cellulosic materials.I. High thermal conductivity and diffusivity *IMA Journal of Applied Mathematics* 49: 273-291.
- Strehlew, R.A., (1985) *Combustion Fundamentals* McGraw-Hill Book Company Inc, New York.
- Steinfeld, J.I., Francisco, J.S. and Hase, W.L., (1989) *Chemical Kinetics and Dynamics* Prentice-Hall Inc, New Jersey.
- Stott, J.B., (1960) Influence of Moisture on the Spontaneous Heating of Coal *Nature*: 186: 54.
- Stott, J.B., (1955) An isothermal micro-calorimeter *Journal of Scientific Instruments*: 33: 58-63.
- Takeno, T. and Sato, K., (1980) Effect of Oxygen Diffusion on Ignition and extinction of Self-Heating Porous Bodies *Combustion and Flame*: 38: 75-87.
- Thomas, P.H., (1980) Fires and Flashover in Rooms – A Simplified Theory *Fire safety Journal*: 3, 67-76.
- Thomas, P.H. and Bowes, P.C., (1961) Some aspects of the self-heating and ignition of solid cellulosic materials *British Journal of Physics*: 12: 222-229.
- Thomas, P.H., (1959) Some approximations in the theory of self-heating and thermal explosion *Fire Research Abstracts and Reviews* 1, 143: 833-839.
- Thomas, P.H., (1958) On the thermal conduction equation for the self-heating materials with surface cooling *Transatlantic Faraday Society*, 54: 60-65.
- Tian, A., (1923) Microcalorimeter with compensation by Peltier and Joule effects *Bulletin De La Societe Chimique de France*: 33, 4: 427-429.
- Transport Canada., (1997) Transportation of dangerous goods ACT, Transportation of Dangerous Goods Regulations: part VII.
- Truninger, E., (1929) *Landwirtsch, Jahrb, Schweiz*, 43, 278
- Uehara, Y., Uematsu, H. and Saito, Y., (1978) Thermal Ignition of Calcium Hypochlorite *Combustion and Flame*: 32, 85-94.
- United Nations, New York and Geneva., (1995) *Transport of Dangerous Goods and Materials, Manual of Tests and Criteria*.
- United States Department of Agriculture., (1977) *Cotton Ginners Handbook* Agricultural Handbook No. 503, Washington D.C.
- United States Department of Transport., (1998) *Code of Federal Regulations, Hazardous Materials*: Title 49, Part 173.
- Walker, I.K., (1980) The heat balance in spontaneous ignition. 10. Linear temperature coefficient of thermal conductivity *New Zealand Journal of Science*: 23: 289-292.
- Walker, I.K., (1967) The Role of Water in Spontaneous Combustion of Solids *Fire Research Abstracts and Reviews*: 9, 15: 5-22.

Walker, I.K. and Harrison, W.J., (1983) Spontaneous ignition of spent brewing grains \*3, Exothermic oxidation at a low oxygen concentration rate *New Zealand Journal of Science*: 26: 33-38.

Walker, I.K. and Harrison, W.J., (1960a) Spontaneous Ignition of Wool III. Calorimetry of Slow Oxidation Reactions in materials of Low Thermal Conductivity *Journal of Applied Chemistry*: 10: 266-276.

Walker, I.K. and Harrison, W.J., (1960b) The Self-Heating of Wet Wool, *New Zealand Journal of Agricultural Research*: 3, 6: 861-895.

Walker, I.K., Jackson, F.H. and Wake, G.C., (1978) Significance of temperature coefficient of reaction rate *New Zealand Journal of Science*: 21, 537-46.

Walker, I.K. and Jackson, F.H., (1958) The heat balance in spontaneous ignition. 5. Influence of sample shape for reactions of zero order *New Zealand Journal of Science*: 12, 302-23.

Wojtowicz, J.A., (1987) Comments on the paper given by V J Clancy at University of Manchester June 16 1987 see [Clancy VJ (1987), Gray, B.F., Holleyhead, R., and Halliburton, B.W., (2000)]

Wexler, A.S. and Seinfeld, J.H., (1991) *Atmospheric Environment* : 25A, 2731.

Zeldovich, Y.B., Barenblatt, G.I., Librovich, V.B. and Makhviladze, G.M., (1985) *The Mathematical Theory of Combustion and Explosions* Academy of Sciences of the USSR, Moscow.