

ANALYSIS OF A BATCH PROCESS EXPLOSION

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An explosion occurred in a batch exothermic reactor when, after approximately 25,000 batches had been carried out successfully over a period of twenty years, one reaction suddenly went out of control resulting in extensive damage to plant and buildings. An investigation into the cause of the explosion was initiated and the resulting plant and kinetic studies are presented here in detail together with the modifications incorporated to allow future batches to be carried out in safety.

INTRODUCTION

Many examples occur in the Chemical Industry where exothermic batch reactions are carried out in which all the reactants and any catalyst are added together and heat applied to initiate the reaction. In such reactions a dangerous situation can rapidly arise if the reaction temperature increases for any reason while there is a large quantity of unreacted material present. This is because as the temperature rises, the reaction velocity and consequently the heat release from the reaction increases exponentially according to the Arrhenius equation. However, the heat removal from the reactor generally only increases linearly being proportional to the temperature difference. Consequently, for such reactions there is a temperature above which heat release exceeds heat removal such that the reaction can go out of control.

This paper considers an incident involving such a batch exothermic reaction. The reaction had been carried out over a period of approximately twenty years during which period the plant had been extended to include seven reactors. During this time it is estimated that approximately 25,000 batches must have been made. The reaction was considered to be somewhat vigorous on start-up and care was always exercised at this stage of the reaction. There had been no previous incident of any note until the one under review. In this, a violent reaction occurred at the start of one of the batches resulting in an explosion in the reactor which was quickly followed by a fire. Extensive damage resulted to both equipment and building but fortunately with no personnel injury. The subsequent consideration and modification of the process is presented here to help others to avoid similar incidents.

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PROCESS DESCRIPTION

Reaction

The reaction system involved is complex being heterogeneous and consisting of three phases, (a) an organic phase containing the majority of the organic feedstock and product, (b) an aqueous phase, and (c) a solid phase comprising a solid reactant. The solid reactant is soluble in water but essentially insoluble in the organic phase. Consequently a solvent is added, soluble in both the organic and the aqueous phase, to improve the contact efficiency across the organic/aqueous boundary for the solid and organic reactants. The solvent also serves to remove some of the heat of reaction from the system by being vaporised and subsequently condensed away from the reactor.

The reactor charge per batch is:

organic feedstock	785 kg
solid reactant	310 kg
solvent	325 kg
water	80 kg

Method Of Operation

The organic feedstock was held on a separate producing plant in a 30m³ capacity storage tank and analysed daily. Material for this reaction would then be weighed into drums, two drums being sufficient for one reactor charge. The solvent was received in road tankers and likewise stored in a 30 m³ capacity mild steel tank. Each solvent delivery was analysed prior to acceptance. The solid reactant was received in drums. Certificates of analysis were received with each consignment and no further testing was normally carried out on site.

The operating procedure for each batch was as follows. The solvent would be pumped to a meter head tank from which the excess overflowed back to storage. The organic feedstock would be charged to a second meter head tank by applying vacuum to the tank and sucking the preweighed charge from the two drums. When these drums had been charged, the solvent would be run in from the first meter tank in order to mix with the organic feedstock. The man-lid on the reactor, a 2.3 m³ glass-lined reactor with anchor-type stirrer, would be opened and 0.08 m³ of water added. To this, half of the solids would be added via the manhole. The solvent/organic feedstock mix would next be run into the reactor and the stirrer started. The remaining solids would then be added to complete the charge and the man-lid closed and secured.

At this stage, steam would be put on to the reactor jacket and the temperature raised. When vapour began to be evolved, as indicated by a rise in temperature of the vapour line adjacent to the reactor, the steam would be turned off, the jacket vented and cooling water applied. The usual time for steam heating was between 15 and 30 minutes. Once reacting, solvent would reflux up the vapour pipe which consisted of a 230 mm diameter column packed with 50 mm Lessing rings surmounted by two in-line 305 mm glass condensers. Condensate ran through a distributor back through the packed column into the reactor.

The refluxing usually died down after about 1 to 1½ hours and the cooling water to the reactor jacket would then be isolated, although the jacket would be left full of water. After a further ½ hour, the jacket would be drained

and steam put on the reactor for about 10 hours to take the reaction to the required degree of completion. At the end of the batch, the reactor contents would be pumped away for further processing.

Detailed Description Of Reactors

At the time of the explosion there was a total of seven reactors, numbered 1 to 7, on this product and all of which were housed in one building. Reactors 6 and 7 were both 2.3 m³ glass-lined jacketed reactors with glass-lined covers and stirrers. The remaining reactors, numbers 1 to 5, were older 2.3 m³ jacketed reactors and consisted of glass-lined reactor bottom sections and stirrers, but with cast iron covers.

Each reactor was fitted with a 230 mm diameter mild steel vapour pipe having a perforated packing support plate and being filled with 50 mm diameter Lessing rings. On reactors 6 and 7 the vapour pipe was attached to a 204 mm diameter branch on the glass-lined cover. On reactors 1 to 5, however, the largest branch size was 100 mm and this was fitted with a spacer to take the diameter up to that of the vapour pipe. In each case, fitted to the top of the vapour pipe, were two 305 mm diameter glass condensers having a total heat transfer area of 5 m². The tops of these condensers were connected by a glass reducer to a 76 mm polypropylene vent. No pressure relief device was fitted to the reactor or the vapour line.

All reactors were fitted with flameproof motors. All starters were non-flameproof but of the oil immersed type. Lighting in the building was flameproof with switches external to the building.

THE EXPLOSION

Eyewitness Reports

As far as could be ascertained, the procedure prior to the explosion was as follows.

All analyses of raw materials had been carried out in accordance with the standard practice with no abnormalities in the results. The No. 2 process operator charged the fourth reactor normally, completing at approximately 12.25 hours. However, instead of carrying out the standard procedure at this stage of applying heat, because of the time he placed cooling water on the jacket and left the building for lunch. He returned at approximately 13.10 hours with the No. 1 operator and explained the state of all the reactors. The No. 2 operator then left the building again, this time to collect his wages.

The No. 1 operator began to start up the reactor by turning off the cooling water, draining the jacket and applying the steam. By approximately 13.20 hours the required temperature in the vapour pipe was reached. The steam in the vessel jacket was then vented and cooling water applied. At this stage the reaction appeared normal. A few minutes later, however, the reaction was reported to have become vigorous as seen by condensate flooding the glass condensers. Three maintenance men in the building were instructed to leave the building and at this stage the plant foreman arrived, attracted by the presence of fume in the atmosphere outside the building.

Both the No. 1 operator and the foreman reported a cessation of the vigorous reaction at this stage, followed by a surge of pressure and a mechanical grating. Both men immediately left the area and on reaching the doorway of the building heard a violent explosion which was rapidly followed

by a fire.

A number of people working outside the building reported a fine spray of liquid in the air before the explosion. Also one of the maintenance men working in the building at the commencement of the reaction, an electrician, reported liquid bubbling in the condensers and liquid dropping on to the staging.

Extent Of Explosion

Examination of the plant following the explosion and fire, showed that the cast iron cover of the number 4 reactor had fractured. The manhole branch had separated and a considerable portion of the lid was also ruptured with a number of pieces having been blown out of the building. The stirrer had been blown out of the reactor and the electric motor separated. Most of the glass heat exchangers in the building were fractured, either by flying debris from the reactor cover or from the fire hoses subsequently played on the burning plant.

The building itself suffered considerable fire damage. The roof had aggravated the problem, being made of a bitumen-coated material. Also a number of platforms within the building were fabricated from wood and consequently caught fire.

Possible Causes

Following the explosion a number of hypotheses were put forward, some of which are presented below.

- a) The explosion was a result of adding incorrect raw materials to the reactor and/or some extraneous reaction.
 - b) Due to a more vigorous reaction than usual, solvent vapours (flammable in air) were boiled out of the vent pipe and/or leaked through the stirrer gland and were ignited by some external ignition source, flashing back into the reactor and causing it to explode.
 - c) A significant variation on this particular batch was that the reactor contents were stirred for approximately 45 minutes prior to starting the reaction. This extra stirring may have presented the opportunity for more of the solid to dissolve in the aqueous phase presenting a higher concentration for immediate reaction or possibly producing a degradation of particle size hence presenting a larger surface area for reaction.
 - d) Incorrect quantities of reactants added causing an increased reaction rate.
- or
- e) Delay in converting from steam heating to cooling may have resulted in additional heat being applied to the reactor at a time when cooling was required.

Consideration will be given to these hypotheses below.

INVESTIGATION INTO THE CAUSE OF THE EXPLOSION

Study Of Plant And Process Operation

Following the explosion, an investigation was made on site. Samples from the original raw materials were collected as far as possible and re-analysed without finding any abnormalities. A considerable quantity of liquid was found still left in the reactor and organic layer was examined by gas liquid chromatography. The only peaks found on the trace were those of the organic feedstock and the finished product. These were in the ratio of 96:4 tending to indicate that the reaction had not progressed very far. Thus, no evidence could be found to support hypotheses (a). Insofar as they could be checked, no discrepancies were found in the weights charged to the reactor.

It was found that a malpractice had crept into the process operation on site. The process operators had found it easier to add the water to the reactor from an adjacent hosepipe. Thus, on occasions, the water charge was added to the reactor via the man-lid, the volume being gauged by eye. Consequently, there was an opportunity to have differing quantities of water in each batch. The effect of such variations on the reaction was unknown. A further feature of the process as operated, was that the change from steam heating to water cooling was determined by the operator assessing the temperature of the vapour pipe by the feel to the hand. (This practice had developed due to poor response times being obtained from measuring elements in glass-lined thermometer pockets and thus a greater reliance on the sense of touch). This must have been a qualitative measurement and unlikely to be consistent between operators.

With respect to the equipment itself, it was found that no design calculations had been retained for the units, the design of which in part appearing to have evolved over the twenty years of operation. The origin for the use of cast iron covers on otherwise glass-lined reactors was unknown, the newer reactors having glass-lined lids. The 100 mm diameter maximum branch size on the cast iron covers would obviously place a considerable resistance on the flow of vapour leaving the reactor against the countercurrent flow of returning reflux. One other unusual feature of the unit was the packing of the vapour pipe with ceramic rings. Since the unit operated on total reflux and no rectification of the vapour was required, the packed section had no function. It would, however, again provide a resistance to the vapour flow.

It is possible to show by simple calculation that the unit was operating near a point of instability as follows:-

Heat given out by reaction. The heat of reaction has been calculated at 905 kJ/kg. From laboratory work presented later, the average conversion over the first 30 minutes of the reaction is 0.9%/minute. Thus with an initial organic feedstock charge of 785 kg, the amount reacting per second is 0.118 kg.

Therefore, the heat evolution is $905 \times 0.118 \times 1000 = 106,790 \text{ W}$

Cooling capacity available. At the time of the explosion, cooling was available for the reaction from the reactor jacket and the vapour condensers. The cooling potential was therefore:-

- a) Reactor Jacket. Perry (1950) gives heat transfer coefficients of between 245 to 400 $\text{W/m}^2 \text{ K}$ for hot water to warm water in unstirred glass-lined reactors. A heat transfer coefficient of 340 $\text{W/m}^2 \text{ K}$ was

assumed.

The relative constants were:

Heat transfer area of jacket 7.3 m^2
Temperature of reaction 69°C
Cooling water assumed to enter at 25°C and leave at 30°C .

Therefore cooling available from the jacket =
 $340 \times 7.3 \times (69-27.5) = 103,000 \text{ W}$

- b) Vapour Condensers. A heat transfer coefficient of $300 \text{ W/m}^2 \text{ K}$ is given for condensing steam in glass condensers (QVF (1970)). It was assumed that the coefficient for condensing solvent was $200 \text{ W/m}^2 \text{ K}$.

Heat transfer area available 5 m^2
Maximum temperature of condensation 69°C
Cooling water as before, entering at 25°C and leaving at 30°C .

Therefore maximum condensation load available =
 $5 \times 200 \times (69-27.5) = 41,500 \text{ W}$

Therefore the maximum cooling rate available was approximately $145,000 \text{ W}$.

From the nature of this calculation, however, the accuracy of the calculated figure is unlikely to be better than $\pm 30\%$.

Flooding point of packed column. Under the conditions of operation, assuming total reflux, the flooding velocity was calculated as 2.3 m/s . On the basis of a 0.23 m diameter column, a vapour density of 1.20 kg/m^3 and a latent heat of 1100 kJ/kg , this was equivalent to a heat load of approximately $128,000 \text{ W}$.

Summarising the calculations:

Normal heat evolved from the reaction, approximately $107,000 \text{ W}$
Heat removal potential of the system, approximately $145,000 \text{ W}$
of which the jacket contributes $103,000 \text{ W}$
Flooding of the column occurs at a heat load of $128,000 \text{ W}$

From these results, it can be seen that the heat evolution required to flood the column was nearly the same as the average heat evolution of the reaction. Also, the total heat removal potential of the reaction system was only approximately 35% above the normal heat evolution of the reaction assuming that the steam had been turned off and cooling water applied to the jacket. Thus, the most likely cause for the start of a build-up of pressure in the reactor appears to be the flooding of the packed column. This would also tend to prevent reflux from returning back to the reactor.

Chemistry Of Process

Although the process had been in operation for about 20 years, no details of the original development work on the process were available nor had any significant amount of experimental work been carried out in the recent years on this particular route. Consequently, following the explosion a considerable amount of work was carried out to gain an insight into the reaction and provide information for subsequent redesign of the reaction system.

Kinetic model of reaction. As stated before, the reaction is heterogeneous and consists of three phases:

- i) an organic phase consisting of the organic feedstock and product, solvent together with any associated water and dissolved solid reactant.
- ii) an aqueous phase consisting of water and solvent together with dissolved solid and organics.
- iii) a solid phase.

Based on these phases, a simplified equation for the overall consumption of organic feedstock might be expressed as

$$\frac{-d(F)}{dt} = M_1 \cdot \left[K_1 \cdot [S] \cdot [F] \right]_{\text{organic}} + M_2 \cdot \left[K_2 \cdot [S] \cdot [F] \right]_{\text{aqueous}} + \left[K_3 \cdot A \cdot [F] \right]_{\text{solid}} \quad (1)$$

where $[F]$ is the concentration of organic feedstock in the liquid phases

$[S]$ is the concentration of solid reactant in the various phases

A is the surface area of the solid

M_1, M_2 are the molar quantities of the two liquid phases

K_1, K_2, K_3 are various reaction rate constants for the three phases

and (F) representing the total organic feedstock present.

A number of laboratory experiments were carried out to quantify the effect of the individual three phases.

- a) The reaction resulting from the solid phase. Experiments were carried out with various particle sized samples of solid in the presence of the organic feedstock but with no water or solvent in order to identify the rate of reaction and the effect of surface area. The mixture was brought up to refluxing conditions and held there for three hours, after which time the contents were analysed. No product was found indicating that the direct reaction between the solid and the organic phase under these conditions was not significant, i.e. K_3 can be assumed to be zero. This, therefore, discounted the possibility of an increased reaction rate due to any degradation of the solids particle size during the prolonged stirring prior to the explosion. The experiment, however, did not examine the effect of solid surface area on dissolution into the aqueous phase nor could any reaction between the solid and the aqueous phase be examined.
- b) A reaction was carried out with organic solid phases only, that is with no water present. After one hour, approximately 25% of the organic feedstock had been consumed indicating that the solid is to some extent soluble in the solvent and confirming that there is a significant reaction in the organic phase between the solid reactant

b) continued.

dissolved in the solvent and the organic feedstock.

c) Laboratory experiments based on the normal method of operation showed an increased conversion with an aqueous phase present. As compared to the 25% conversion after one hour for the organic phase only, a conversion of 41% occurred after 1 hour with a 99.5% conversion after 6 hours.

As a result of these experiments equation (1) can be simplified to:-

$$\frac{-d(F)}{dt} = M_1 \cdot \left[K_1 \cdot [S] \cdot [F] \right]_{\text{organic}} + M_2 \cdot \left[K_2 \cdot [S] \cdot [F] \right]_{\text{aqueous}} \dots \dots \dots (2)$$

A further simplification may also be made for the initial stage of the reaction if it is assumed that the dissolving solid reaches saturation conditions. (This is most likely on the full scale plant since stirring and heating are applied for between 15 and 30 minutes before the reaction starts). Thus, [S] organic and [S] aqueous should be at their saturation and maximum values. Equation (2) then becomes

$$\frac{-d(F)}{dt} = M_1 \cdot \left[K'_1 \cdot [F] \right]_{\text{organic}} + M_2 \cdot \left[K'_2 \cdot [F] \right]_{\text{aqueous}} \dots \dots \dots (3)$$

where K'_1 and K'_2 are modified reaction rate constants.

From experiments (b) and (c) above, both of these phase reactions are important and it is difficult to quantify the results more due to possible changes in the partition coefficient of the solvent as the feedstock/product ratio changes. It should be noted that at the outset of the reaction, [F] aqueous should reach an equilibrium constant value and [F] organic will be a maximum.

Although the rate of reaction will depend on [F] organic and this will reduce as the reaction proceeds and the feedstock is replaced by product, since this is only a partial factor the initial rate is likely to be a constant gradually declining with time as [F] organic falls.

Initial rate of reaction. Fig. 1 presents the information obtained by the laboratory simulation of a normal reaction taking time zero to be the start of refluxing. (This may present a false scale during the first few minutes of reaction). It is seen that in this experiment a delay appeared to occur after 15 minutes with only a 7% conversion. When repeated a value of 10% was obtained for the second experiment and hence showed no similar delay. From the curve in Fig. 1 the conversions achieved may be deduced as:-

- over the first 30 minutes, conversion averages 0.9%/minute
- over the first 60 minutes, conversion averages 0.75%/minute
- maximum conversion assuming curve is true, is approximately 1.6%/minute

Also shown in Fig. 1 are the results obtained for a run when the reactants were left stirring for 30 minutes prior to starting the reaction. No peculiarities are in evidence for this situation to support the hypothesis that the long stirring time contributed to the explosion.

These reaction curves, and also later ones presented in Fig. 2, indicate an approximately constant rate of reaction over the first two hours. This tends to discount the possibility of a very vigorous reaction at the start of the batch being a feature of the reaction. It is true that a blip in the reaction curve is in evidence in Fig. 1, although it was not repeated in subsequent runs. Two possibilities might explain this anomaly. One, that it was due to an error in timing or sampling; or two, that stirring in the laboratory was insufficient to obtain the equilibrium value of the solid concentration.

The effect of water on the reaction rate. As mentioned above, a malpractice had crept into the process in that the amount of water charged was not monitored accurately. This could have affected the partition between the two phases and consequently the factors M_1 and M_2 in equation (3) which could lead to changes in reaction rate. Laboratory experiments were therefore carried out to check the significance of such variations.

Fig. 2 shows the effect of water content in the reactor while all other constituents were maintained in the same proportions as on the full scale plant. The curves drawn indicate again an approximately constant rate of conversion over the first 60 to 90 minutes of the reaction. It is seen that the effect of increasing the water over the standard level is to initially increase but then to reduce the conversion. These changes are most likely due to the redistribution of the various constituents between the phases.

These experiments demonstrated that small increases in water content could increase the initial reaction rate, perhaps by up to 15%. This might therefore be a contributing factor towards the more vigorous reaction in the No. 4 reactor but is unlikely in its own right to have been the sole reason for the explosion.

Again, in all these experiments, no reaction was detected until reflux conditions were attained. Also, if a reacting system was cooled below its boiling point, no further reaction could be detected.

CALCULATION OF REACTION UNDER ADIABATIC CONDITIONS

In order to help assess the effect of reacting in a closed unit with no venting potential and also to help in subsequent bursting disc calculations, consideration was given to the reaction under adiabatic conditions. The procedure in general follows the principles given by Boyle (1967).

Rate Of Temperature Rise

The reaction rate can be related to the temperature by the Arrhenius equation which can be expressed as:

$$R = c.e^{aT} \dots \dots \dots (4)$$

where R = conversion rate (%/s)

T = temperature (K)

and a and c are constants.

The rate of reaction over the first 30 minutes was found to be 0.9% per minute. However, a possible maximum rate of 1.6% per minute was indicated and this value is used in the subsequent calculation. These values apply to a reaction temperature of 69 °C and the effect of temperature was not investigated

experimentally. To have altered the reaction temperature would have involved operation under pressure and this was not pursued. It was therefore assumed that 10 °C rise in temperature would result in an increase in the speed of reaction of 2½ times.

Substituting these values in equation (4) gives

$$\frac{1.6}{60} = c.e.^a \cdot (273 + 69) \dots \dots \dots (5)$$

$$\frac{1.6 \times 2.5}{60} = c.e.^a \cdot (273 + 79) \dots \dots \dots (6)$$

Solving these equations gives

$$R = 6.61 \times 10^{-16} e^{0.0916T} \dots \dots \dots (7)$$

Time to complete reaction under adiabatic conditions. When reacting under adiabatic conditions, no heat is being removed from the reactor so all of it is taken up as sensible heat by the reactants.

Then

$$\frac{dT}{dt} = \frac{W_f \cdot \Delta H \cdot R}{W_b \cdot C_p \cdot 100} \dots \dots \dots (8)$$

- where
- t = time (s)
 - W_f = weight of organics feedstock (kg) (= 785)
 - W_b = total weight of batch (kg) (= 1500)
 - ΔH = heat of reaction (kJ/kg) (= 905)
 - C_p = specific heat of liquid (kJ/kg K) (= 2.5)

The conversion rate R will in most cases vary as the reaction proceeds unless the reaction is of zero order. Account could be taken of this, but in the instance considered here the reaction could be considered constant for the greater part of the reaction.

Substituting the values in equation (8) together with equation (7) results in

$$i.e. \frac{dT}{dt} = 1.25 \times 10^{-15} e^{0.0916T} \dots \dots \dots (9)$$

Integrating, the time for complete reaction

$$\Delta t = \int_{T_1}^{T_2} \frac{dT}{1.25 \times 10^{-15} e^{0.0916T}}$$

$$i.e. \Delta t = \left[-8.73 \times 10^{15} e^{-0.0916T} \right]_{T_1}^{T_2} \dots \dots \dots (10)$$

where ΔT is the time required for the adiabatic temperature rise from T_1 to T_2 . The reaction will become explosive (i.e. instantaneous pressure rise) when $T_2 = \infty$ (see(Boyle 1967)). By substituting, $T_2 = \infty$ in equation (10), the time to go from any temperature T_1 to explosion conditions can be calculated:

$$\underline{\Delta t = 8.73 \times 10^{15} e^{-0.0916T_1} \dots \dots \dots (11)}$$

This equation is plotted in Fig. 3 and shows that with a starting temperature of 69 °C and with reaction under adiabatic conditions, complete reaction will occur within 217 seconds. Should the reaction become adiabatic at a higher temperature, say, 100 °C, then complete reaction can occur within the very short period of 13 seconds.

By substituting the starting temperature of 69 °C (i.e. $T_1 = 342$ K) in equation (10), the temperature profile of the reactor under adiabatic conditions can be deduced and is given in Fig. 4. For the reaction conditions here, the maximum temperature rise would be 189 °C, to a final reactor temperature of 258 °C.

The pressure developed in the reactor during such a reaction can be calculated from this using the vapour pressure relationship for the reactor mix (given in Fig. 5) and the results are plotted in Fig. 6.

Table I presents the effect of various conversions of the organic feed-stock to show how the reactor pressure rises. It is not possible to predict the pressure required to fracture the cast iron cover of the reactor but possibly a pressure of 200 kN/m² may have been required. From Table I it is seen that such pressures can be generated by fairly low conversions. The sample of reactants taken from the reactor after the explosion showed only a 4% conversion. According to the calculation this would have generated a pressure of 40 kN/m² which is unlikely to have caused the explosion damage experienced. However, this sample is unlikely to be truly representative but does confirm that the reaction had not progressed very far. Also, the time from the first sign of trouble in the reactor to explosion was assessed by eye-witnesses at a few minutes and consequently fits well with the times in Table I.

Table I - Values for Adiabatic Reaction Time and Reactor Pressure for various Conversion Levels.

Conversion	Adiabatic Reaction Times	Reactor Pressure
4%	110 s	40 kN/m ²
10%	175 s	100 kN/m ²
15%	200 s	180 kN/m ²
20%	210 s	280 kN/m ²

CONCLUSIONS FROM INVESTIGATION

After a plant has been extensively damaged by explosion and fire it is usually difficult to be certain as to the exact cause of the incident. However, the conclusions from the investigation were:

- 1) the correct raw materials had been charged to the reactor and no untoward reaction had taken place

- 2) eyewitnesses report solvent vapour and liquid being present in the building prior to the explosion and that the fire followed the explosion. It is unlikely that sufficient air would have been present in the reactor at that stage in the reaction to support a flashback into the reactor. This hypothesis was therefore discounted.
- 3) although it is possible that the additional stirring prior to the reaction may have contributed to an increased rate of reaction, this was not considered to be the basic cause of the explosion.
- 4) incorrect quantities of water could have been added to the reactor which may have given an increase in reaction rate for this batch.
- 5) it is concluded that the explosion in the reactor was caused by a build-up in pressure started by the flooding of the packed vapour pipe. From the calculations this could have been caused by a delay in changing from steam heating to water cooling, by an obstruction in the cooling water supply, or by a more vigorous reaction than normal. The flooding of the packed column in its own right is unlikely to have built up a pressure sufficient to burst the cast iron cover, the maximum height of liquid trapped being only about 3 m. It was therefore concluded that because of this initial blockage of the vapour venting system from the reactor, either solid reactant was thrown against the packing support plate or the ceramic packing was lifted and crushed against the top distributor completely blocking the reactor vent. The pressure which the lid could withstand is indeterminate due to the poor resistance of cast iron to shock. Calculations do indicate from the time scale involved and the composition of the reactor contents, that a build-up in pressure sufficient to burst the cover would have occurred under adiabatic conditions.

MODIFICATION OF THE PROCESS

Possible Means Of Moderating The Reaction

As stated above, when all the reactants of a batch exothermic reaction are charged at the beginning and steam used to initiate the reaction, then a potentially dangerous situation is present. Because of the need to resume safe production quickly, consideration was given to avoiding this situation by adding reactants continuously in order to limit the reactants available at any time. Unfortunately it was concluded that this was not possible. Although the continuous addition of the organic feedstock would have been advantageous, it was concluded that it would not be possible due to:

- a) it would be very difficult to stir the contents of the reactor with a reduced volume of liquid.
- b) the reaction needs to be under refluxing conditions to proceed. If there was any deficiency of feedstock the reaction could stop and allow reactant quantities to build up until the reaction was initiated again.
- c) it was difficult to see a foolproof system of protection to avoid excess reactants entering the reactor on occasions that would offer advantage over a modified reactor system based on the existing method.

Another means of moderating the reaction could have been by controlling the water addition. Due to the small quantities involved and its complex role, this again was rejected. Continuous addition of solid was also rejected presenting a number of problems outside the scope of this paper.

Plant Modifications

The following modifications were made to ensure subsequent safe working of the process.

- a) The design philosophy adopted was to remove all the heat using a vapour condenser. The glass heat exchangers were replaced by mild steel units rated at 300,000 W. These units are capable of removing all the heat of reaction and any heat input if the steam should be left inadvertently onto the reactor jacket, and also allow a safety margin.
- b) The previous restrictions to vapour flow were removed by increasing nozzle sizes on the reactor covers, removing the packed column sections and adopting separate reflux return lines.
- c) The lids of all reactors were replaced by glass-lined covers rated at 275 kN/m² working pressure.
- d) All reactors were protected by a burster disc fitted to the vapour line giving a direct vertical vent to outside the building. The bursting pressure was set at 66 kN/m². The calculation to check this is given in the Appendix.
- e) The addition of water was to be made only via a meter tank.
- f) The incorporation of a number of alarms and instrumentation.

DISCUSSION

The site on which the process was operated was an old established chemical works at which plants had been developed over a period of many years by a process of evolution from the laboratory scale. Following a change of ownership, the new management recognised that the plant was not up to modern technical and safety standards and a replacement plant based on new technology was designed, authorised and construction put in hand.

Meanwhile it was essential to maintain production of a vital chemical and in view of the many years of successful operation of the plant, it was decided that it should continue in operation until the new plant was ready. The subsequent explosion and the detailed analysis that followed and is the subject of this paper, showed that too much reliance was placed on the skill of the operators and the past history of success when deciding to continue. The moral is that when a process appears to have questionable safety aspects, then it is essential that a vigorous technical analysis should be carried out to provide a sound basis for judgement as to whether to continue to operate the plant. Although this is particularly true when plants are 'inherited', as in this case, considerable process and plant changes can be made during the operating life of a plant. Consequently, regular technical audits are to be encouraged.

With particular reference to batch exothermic reactions, situations should be avoided where all the reactants are added at once especially if heat is necessary to initiate the reaction. Also care is needed when scaling up batch reactors since the heat removal potential to heat release potential will decrease as reactor size increases. Such reactors must always be protected against over-pressure, bearing in mind that the design of such devices must cater for the emergency conditions. As demonstrated here, runaway reaction times can be extremely short and provide little opportunity for operator correction.

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SYMBOLS USED

- A = surface area of solid reactant (m^2)
- a = constant in Arrhenius equation
- c = constant in Arrhenius equation
- C_p = specific heat of liquid (kJ/kg K)
- D = diameter of vent pipe (m)
- [F] = concentration of organic feedstock (%)
- [F] = total organic feedstock quantity
- f = fanning friction factor
- g = gravitational constant (m/s^2)
- ΔH = heat of reaction (kJ/kg)
- $K_1, K_2, K_3, K'_1, K'_2$ = reaction rate constants
- K_c = coefficient of discharge
- M_1, M_2 = molar quantities of liquid reactant phases
- P_1, P_2 = upstream and downstream pressures, respectively, (N/m^2)
- $\Delta P = (P_2 - P_1)$ (N/m^2)
- R = reaction conversion rate (%/s)
- Re = Reynolds number
- [S] = concentration of solid reactant
- T = temperature (K)

T_1, T_2 = initial and final temperatures respectively (K)

t = time (s)

Δt = time interval (s)

\underline{V} = specific volume of fluid (m^3/kg)

V_1, V_2 = vapour velocity in reactor and vent respectively (m/s)

W_b, W_f = total weight of batch and weight of organic feedstock respectively (kg)

W_e = energy losses (m)

Z_1, Z_2 = upstream and downstream elevation respectively (m)

ΔZ = ($Z_2 - Z_1$) (m)

ρ = density (kg/m^3)

μ = viscosity (kg/ms)

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APPENDIX. BURSTING DISC CALCULATION

Due to the ease of availability on site, a 150 mm bursting disc was the most convenient to use for this application in the time period available. The validity of this size of burster was confirmed as below.

The design method adopted was based on a procedure suggested by Boyle (1967) as recommended by H.M.F.I. (1967). Boyle considers the sizing of burster discs for polymerisation reactors and concludes for this situation that vapour venting gives a conservative answer as compared to liquid venting. The article applies to high viscosity liquids where high friction losses can result with liquid flow in the vent pipes. However, in the situation under consideration here, viscosities are low and therefore the situation of liquid venting is likely to provide a conservative answer. For comparison though, the analysis was carried out for both liquid and vapour venting.

Flow through vent pipe

For fluids flowing in pipes, the basic flow equation (see Boyle (1967)) is:

$$\int_{P_1}^{P_2} \frac{V dP}{g} + (Z_2 - Z_1) + \frac{V_2^2 - V_1^2}{2g} = -W_e \quad \dots \dots \dots (12)$$

- where V is the specific volume of fluid (m³/kg)
- P_1 is the upstream, P_2 the downstream pressure (N/m²)
- Z_1 is the upstream, Z_2 the downstream elevation (m)
- V_1 is the upstream, V_2 the downstream fluid velocity (m/s)
- W_e is the energy losses (m)
- g is the gravity constant (9.81 m/s)

By assuming

- a) that an average density can be used over the temperature range involved, and
- b) the upstream velocity, i.e. the velocity within the reactor, is zero

then equation (12) becomes:

$$\frac{\Delta P}{\rho g} + \Delta Z + \frac{V_2^2}{2g} = -W_e \quad \dots \dots \dots (13)$$

where $\Delta P = P_2 - P_1$ and equals the burst pressure of the disc (N/m²)

ρ is the density of the vent fluid (kg/m³)

ΔZ is the vertical height of the vent, and equals $Z_2 - Z_1$ (m)

The energy loss, W_e , results from friction in the vent pipe and from the sudden contraction of vapours when entering the vent pipe and is given, (see Boyle

(1967)), by:

$$W_e = \frac{4f \Delta Z}{D} \cdot \frac{V_2^2}{2g} + K_c \frac{V_2^2}{2g} \dots \dots \dots (14)$$

where D is the diameter of the relief pipe (m)

f is the friction factor

K_c is the coefficient of discharge

Combining equations (13) and (14) yields:

$$\left(\frac{4f \Delta Z}{D} + K_c + 1.0 \right) \frac{V_2^2}{2g} = \frac{\Delta P}{\rho g} - \Delta Z \dots \dots \dots (15)$$

For analysis of the system, the following constants were taken:

- Z = 5 m The length of vent pipe
- D = 0.15 m 150 mm burster disc and vent pipe
- K_c = 0.41 Since turbulent flow conditions
- ΔP = 66,000 N/m² Burster pressure rating

Therefore, equation (15) becomes:

$$V_2^2 (6.80 f + 0.0719) = \frac{6728}{\rho} - 5 \dots \dots \dots (16)$$

The friction factor is dependent upon the Reynolds number, Re,

$$Re = \frac{DV_2 \rho}{\mu} = \frac{0.15 V_2 \rho}{\mu} \dots \dots \dots (17)$$

where the viscosity, μ, is in kg/ms

Liquid Venting

Liquid conditions on venting were assumed as follows:

- Density = 1250 kg/m³
- Viscosity = 1 c.p. ≡ 1 x 10⁻³ kg/ms

Therefore equation (17) reduces to

$$Re = 187,500 V_2 \dots \dots \dots (18)$$

Equation (16) becomes

$$V_2 = \sqrt{\frac{0.3824}{6.80 f + 0.0719}} \dots \dots \dots (19)$$

Solving equations (18) and (19) for V₂ using standard friction factor charts, the vent velocity, V₂, was found to be 1.95 m/s.

$$\text{Area of vent pipe} = 0.0177\text{m}^2$$

$$\text{Vent capacity} = 0.0345 \text{ m}^3/\text{s}$$

$$\text{Total capacity of vessel contents} = 1.2 \text{ m}^3$$

$$\text{Therefore, time to vent} = \frac{1.2}{0.0345} = 34.8 \text{ seconds}$$

Time to vent entire contents as liquid is 35 seconds

Vapour Venting

Should the bursting disc blow, the pressure in the reactor would be 66 kN/m^2 which from Fig. 5 would indicate a reactor temperature of 81.5°C . In this situation where vapour venting is occurring, the solvent will be preferentially vented from the reactor. The vent handling capacity from pressure drop considerations can be evaluated in a similar way as for liquid venting.

With the physical properties as:

$$\text{vapour density } 1.75 \text{ kg/m}^3$$

$$\text{vapour viscosity assumed at } 0.011 \text{ cp,}$$

then the vent handling capacity is $3.6 \text{ m}^3/\text{s}$.

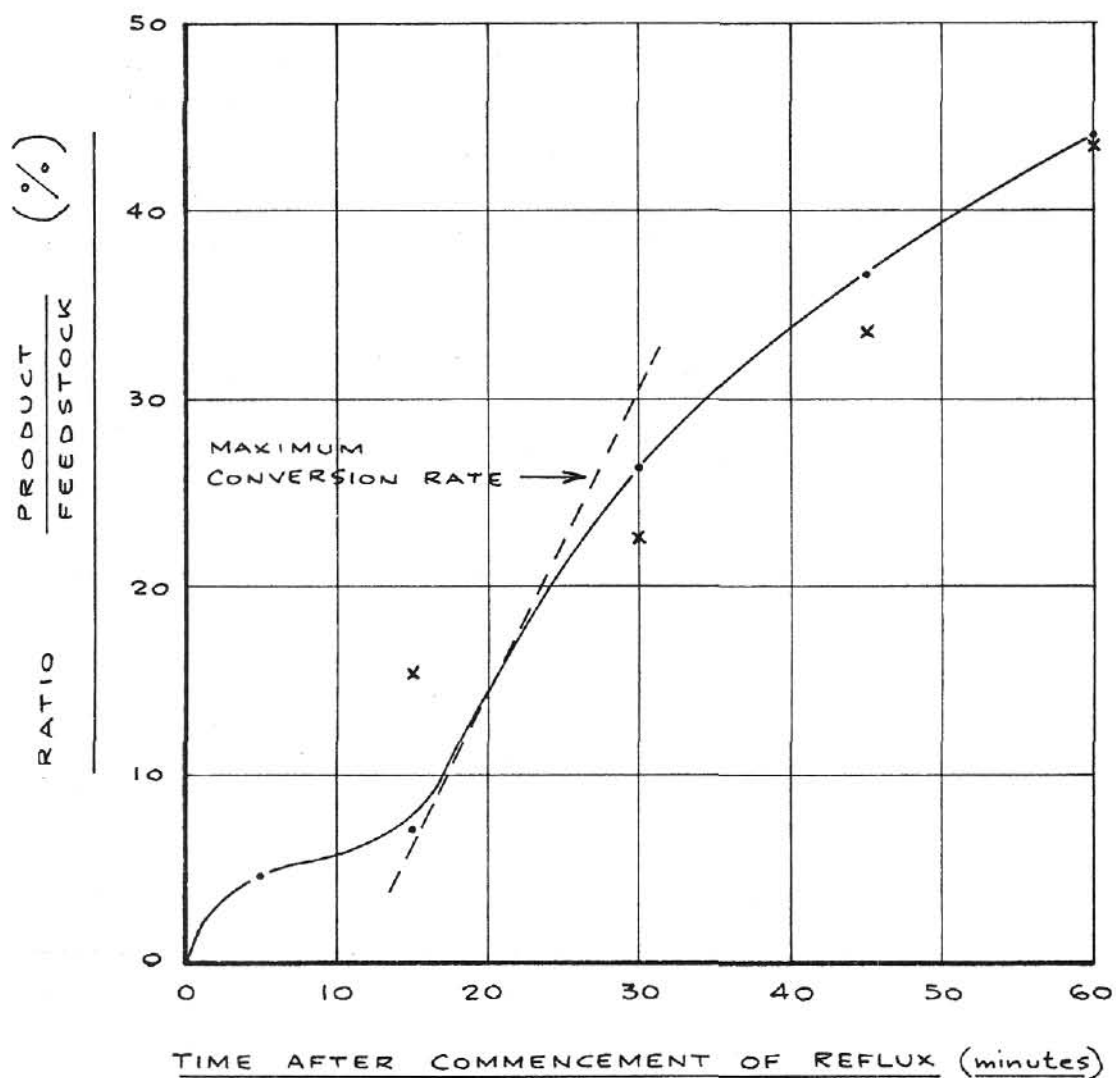
However, as vapour is lost from the system, it takes with it its heat of vaporisation. Now at 81.5°C , the heat liberated

$$= W_f \Delta H R/100$$

$$= 785 \times 905 \times 6.61 \times 10^{-16} e^{0.0916(273 + 81.5)}$$

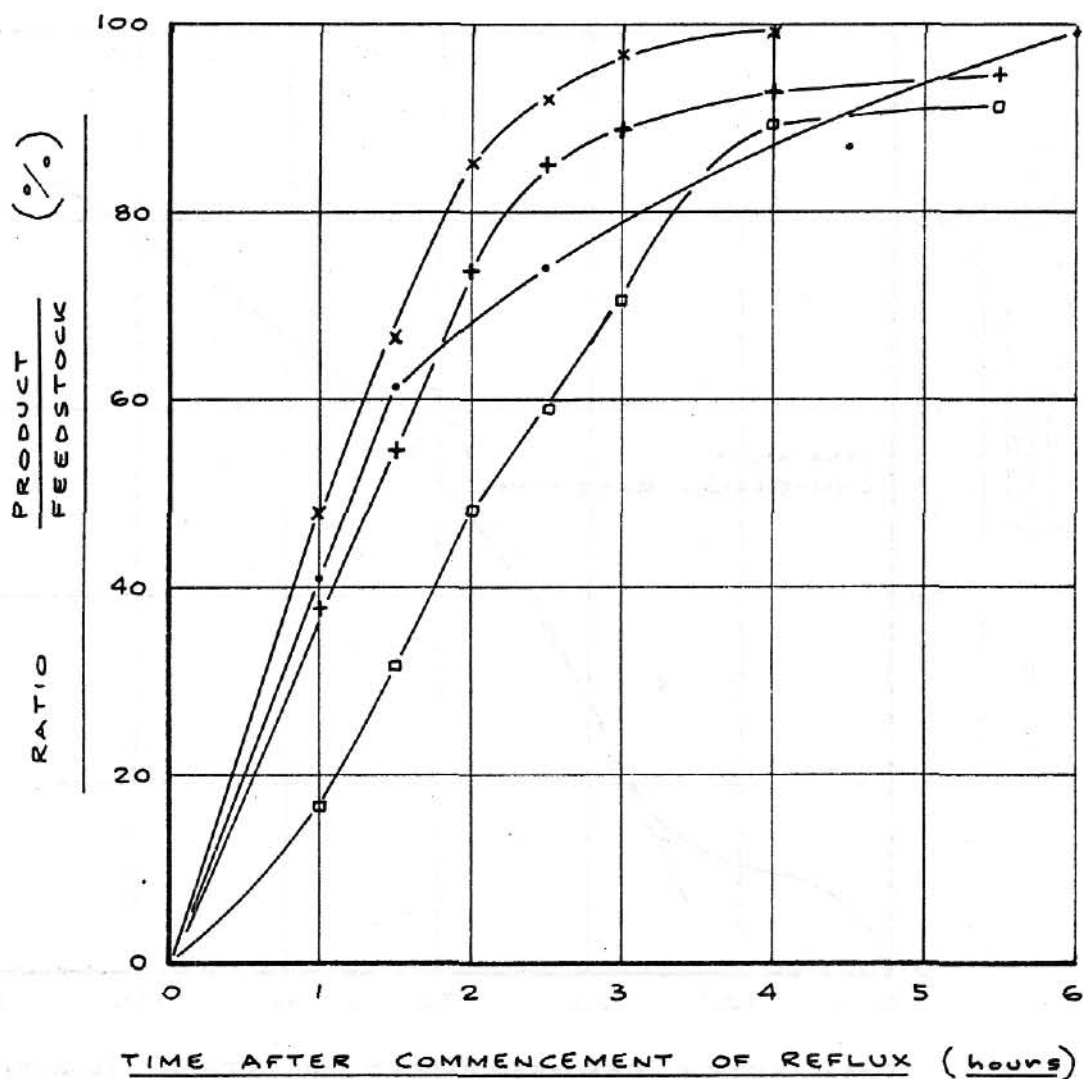
$$= 595 \text{ kJ/s}$$

Taking the vapour latent heat as 1100 kJ/kg yields a vapour generation rate of $0.31 \text{ m}^3/\text{s}$. Since the vapour generation rate is less than the vent handling capacity, the pressure in the reactor will fall once the bursting disc has been ruptured and hence the selected disc is suitable for this duty.



• SIMULATION OF NORMAL OPERATION
 x DELAY OF 30 minutes BEFORE STARTING REACTION

FIG.1 . GRAPH OF PRODUCT PERCENTAGE AGAINST TIME OF REACTION.



- 50% OF STANDARD WATER CHARGE
- x 150% OF STANDARD WATER CHARGE
- + 200% OF STANDARD WATER CHARGE
- 250% OF STANDARD WATER CHARGE

FIG. 2. GRAPH OF PRODUCT PERCENTAGE
AGAINST TIME OF REACTION
FOR VARYING WATER CONTENTS.

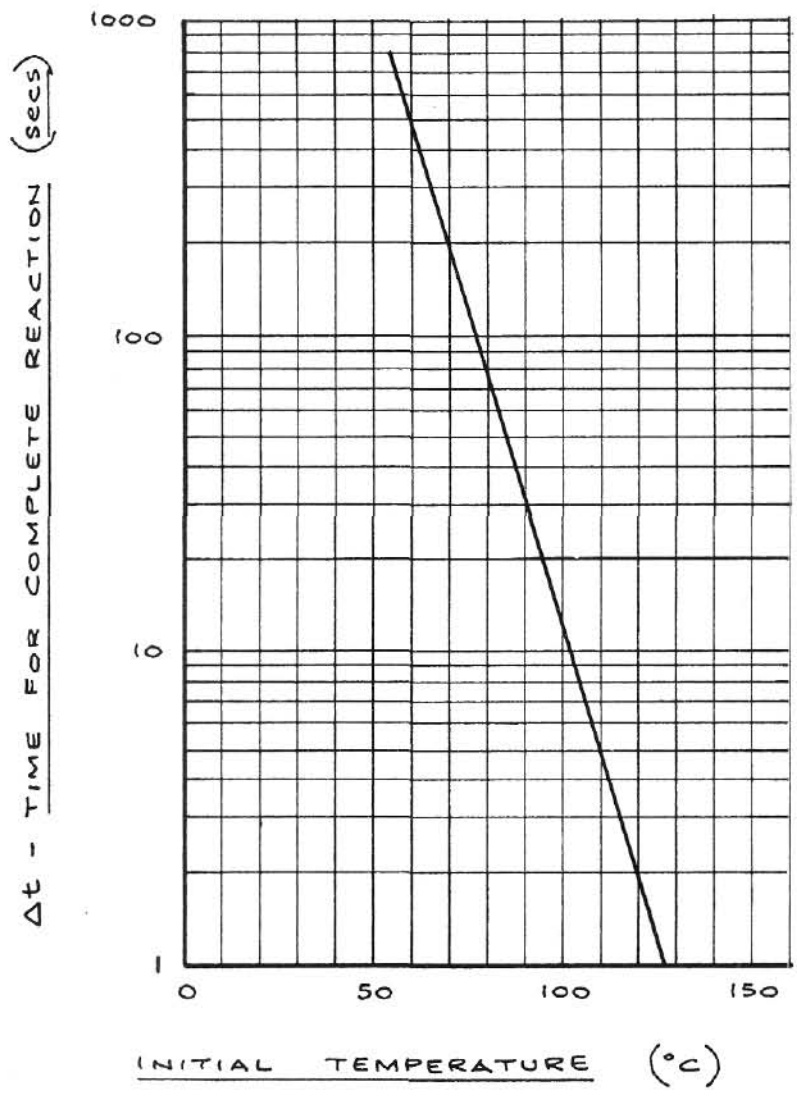


FIG. 3. GRAPH OF TIME FOR COMPLETE
REACTION UNDER ADIABATIC CONDITIONS
AGAINST INITIAL TEMPERATURE

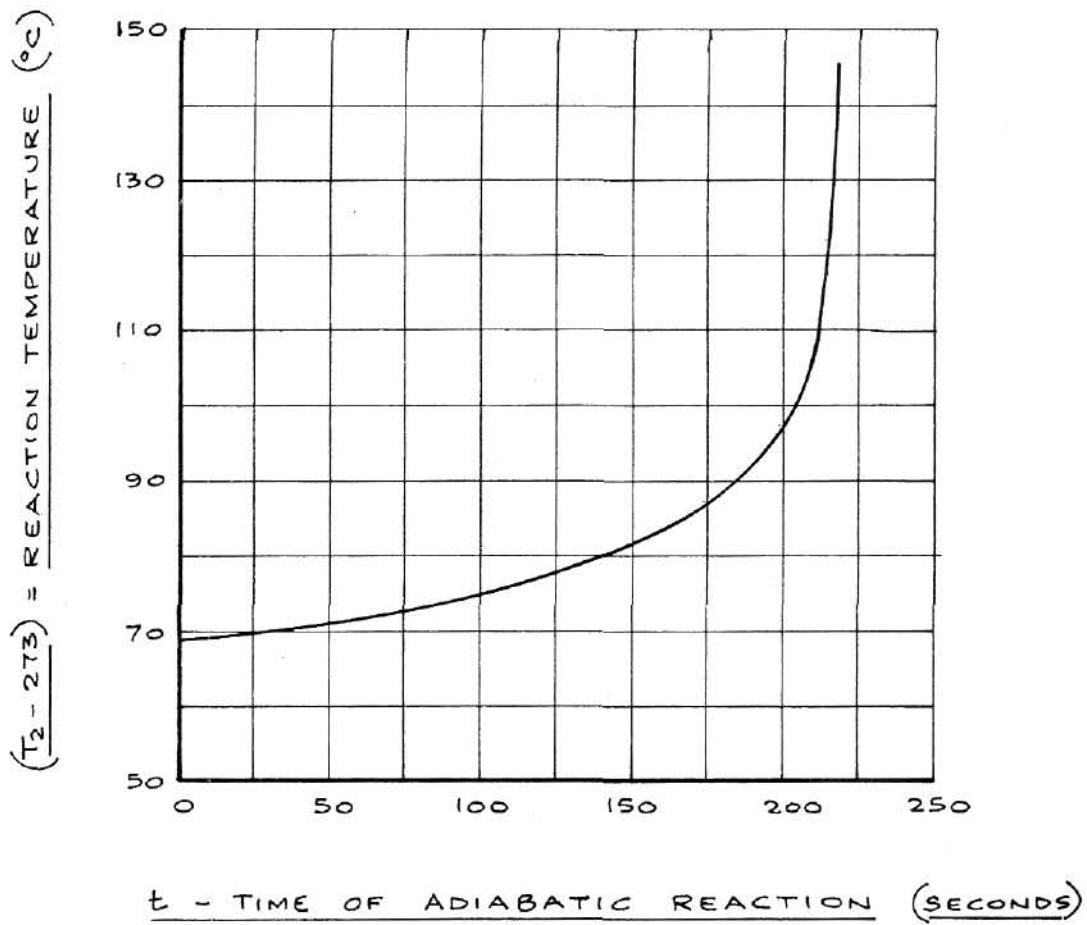
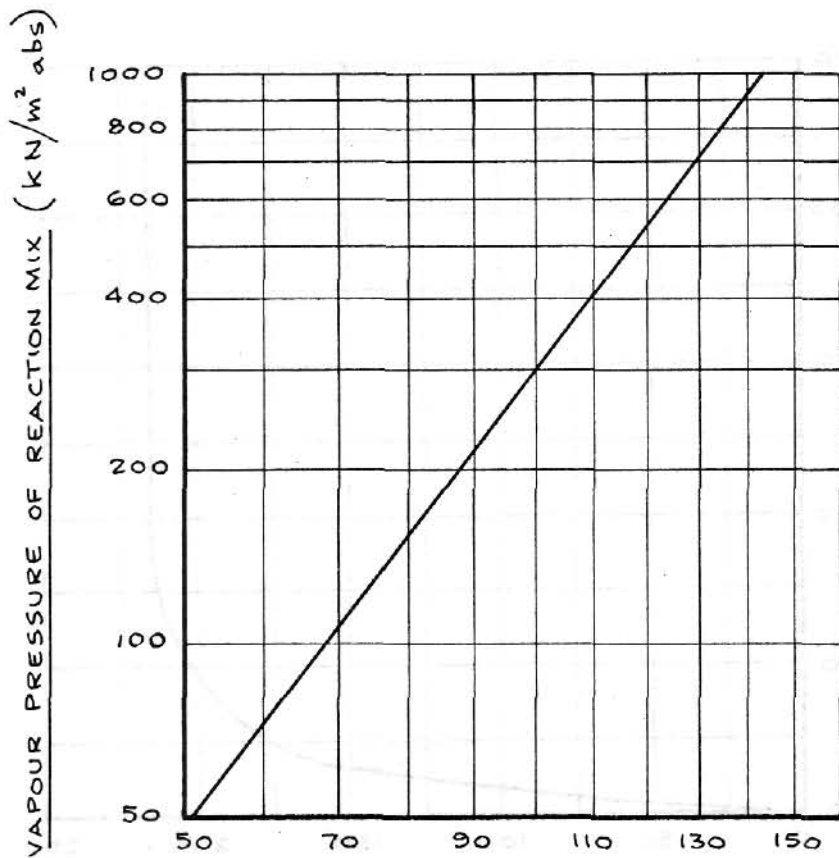


FIG. 4. PLOT OF REACTION TEMPERATURE
AGAINST TIME FOR REACTION
UNDER ADIABATIC CONDITIONS.



TEMPERATURE OF REACTION MIX ($^{\circ}\text{C}$)

FIG. 5. VAPOUR PRESSURE CURVE
FOR REACTION MIX.

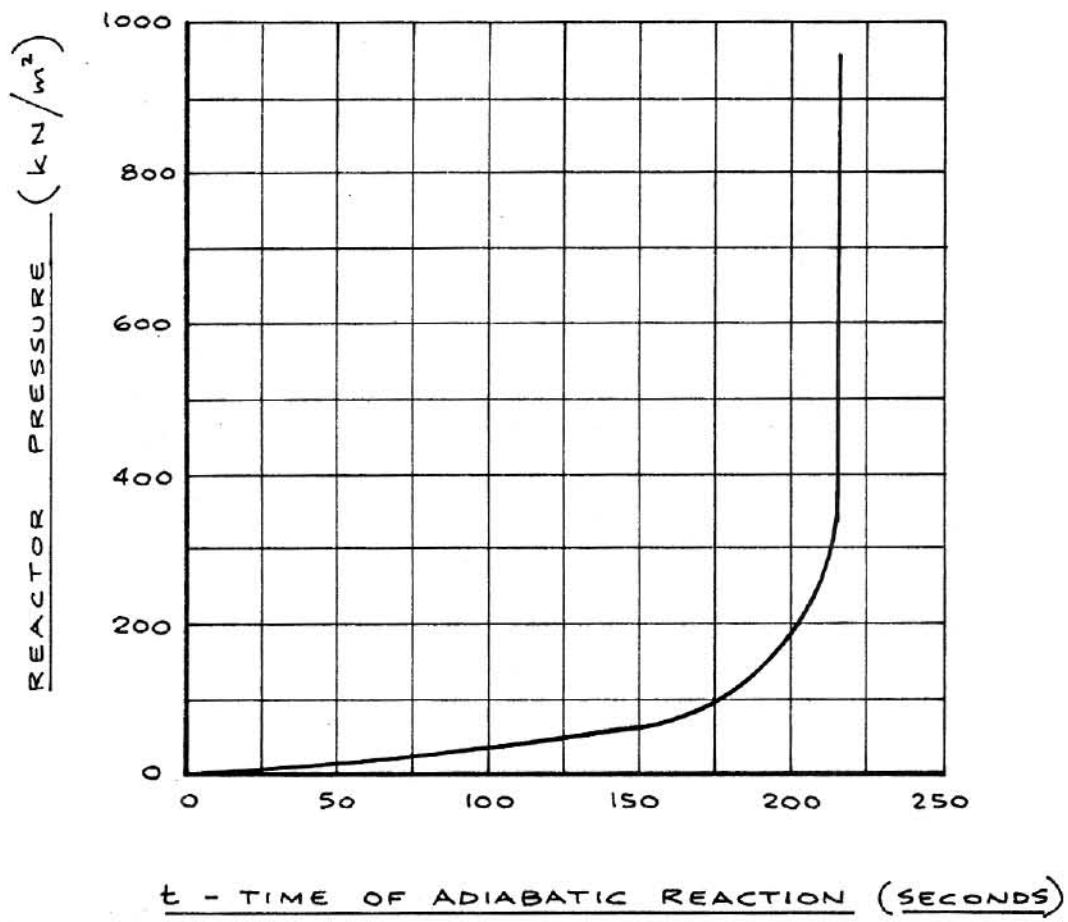


FIG.6 PLOT OF REACTOR PRESSURE
AGAINST TIME FOR REACTION
UNDER ADIABATIC CONDITIONS.