

## THE SEVESO CASE AND THE SAFETY PROBLEM IN THE PRODUCTION OF 2,4,5-TRICHLOROPHENOL

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(Received June 15, 1984; accepted June 29, 1984)

### Summary

Extensive investigations of the "Seveso mixture" by advanced thermoanalytical techniques and engineering experiments allow an explanation of the Seveso accident and a definition of the criteria for conduction of the process for the production of 2,4,5-trichlorophenol. A critical comparison of the process in methanol and in ethylene glycol as reaction medium points to the latter as being more controllable and consequently safer.

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### Introduction

The Seveso accident has met with great interest in the scientific world, also because of the difficulties experienced in finding out the reasons of the rupture of the bursting disk in the ICMESA reactor on July 10th, 1976 [1–10]. It has probably never happened in the past that such an effort was made to understand, from a physico-chemical point of view, an accident occurring in a chemical plant.

A convincing description of the likely mechanism of the accident was eventually proposed at meetings in London in March 1981 [11, 12], in Milan in June 1982 [13], and elsewhere [14, 15]. This new and somewhat surprising mechanism was considered in scientific papers [6, 12, 15, 16], and complete results of the studies carried out on this problem have been published now [17–19]. Other measurements of the thermal stability of the "Seveso mixture" [20–24] led to a better understanding of the safety problems in the production of 2,4,5-trichlorophenol (TCP).

These different pieces of information are now firmly established and make it possible to interpret the Seveso accident and also previous accidents which occurred during the production of TCP.

## The ICMESA accident

It might be useful to remember that the accident occurred in a plant producing TCP from 1,2,4,5-tetrachlorobenzene and NaOH at atmospheric pressure in the presence of ethylene glycol as reaction medium. In this process the alkaline hydrolysis of tetrachlorobenzene\* (exothermic reaction), carried out at 140–160°C, was followed by distillation of the ethylene glycol\*\* under vacuum at 140–170°C.

At the beginning of the operation, 3235 kg of ethylene glycol, 603 kg of xylene, 2000 kg of 1,2,4,5-tetrachlorobenzene and 1100 kg of caustic soda were charged into the reactor, which had a capacity of 10 m<sup>3</sup>.

In the morning of the day when the accident happened, after the hydrolysis step, when presumably about 15% of the ethylene glycol initially charged had been distilled, heating by steam was discontinued and vacuum was terminated by connection of the reactor to the atmosphere (with consequent air inlet in the reactor). Stirring was maintained during 15 minutes, then all operations were stopped [2]. At that time the reaction mixture was at about 158°C and the wet part of the reactor wall was at the same temperature as the liquid; the upper, dry part of the wall was, at least partially, at about 300°C [18]. In fact, steam at 12 bar (condensation temperature 190°C) was used, but this steam arrived superheated, at about 300°C, at the upper part of the coil welded to the outside wall of the reactor [17]. The bursting disk, set at 4 bar, ruptured seven and a half hours after operation was discontinued. The temperature profile during the operation and after the accident is shown in Fig. 1 [8, 9].

According to the literature until 1976, and on the basis of differential thermal analysis [25], chlorophenols and alkali chlorophenates should not show phenomena of instability, according to their nature, below 250–300°C. The hydrolysates obtained in the production of TCP were known to show uncontrollable exothermic behaviour at about 230°C, after ethylene glycol removal [26]. Yet, these processes had been ascribed to decomposition of the monosodium derivative of ethylene glycol (NaOCH<sub>2</sub>CH<sub>2</sub>OH) and not to decomposition of sodium trichlorophenate.

According to a patent [27] on the preparation of TCP in the presence of methanol, uncontrollable reactions may develop during the alkaline hydrolysis within the temperature range 165–180°C. Finally, another patent [28] on the same process in ethylene glycol with ethylene glycol/tetrachlorobenzene molar ratios lower than 5\*\*\* mentions uncontrollable exothermic

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\*During this step the reaction water is continuously distilled as an azeotrope with xylene. In spite of the exothermicity of the reaction, this step needs external heating.

\*\*During the hydrolysis about 50% of the initially charged glycol condenses to diethylene glycol, which is not distilled with the monoethylene glycol in the following distillation step.

\*\*\*In the ICMESA process this ratio was 5.6 and the glycol + xylene/tetrachlorobenzene ratio 6.5.

reactions that would already take place during hydrolysis at a temperature slightly above  $150^{\circ}\text{C}$ . However, experiments carried out by one of us [29] demonstrated that the experimental data of this patent were unreliable. The example of this patent was repeated under identical conditions in our laboratory. In contrast with the statement "after initial water and xylene removal at a temperature of  $155^{\circ}\text{C}$  instead of  $160^{\circ}\text{C}$  the reaction medium became exothermic and the temperature rose to  $250^{\circ}\text{C}$  within five seconds" the mixture kept at  $155^{\circ}\text{C}$  for 4 hours did not show any exothermic reaction.

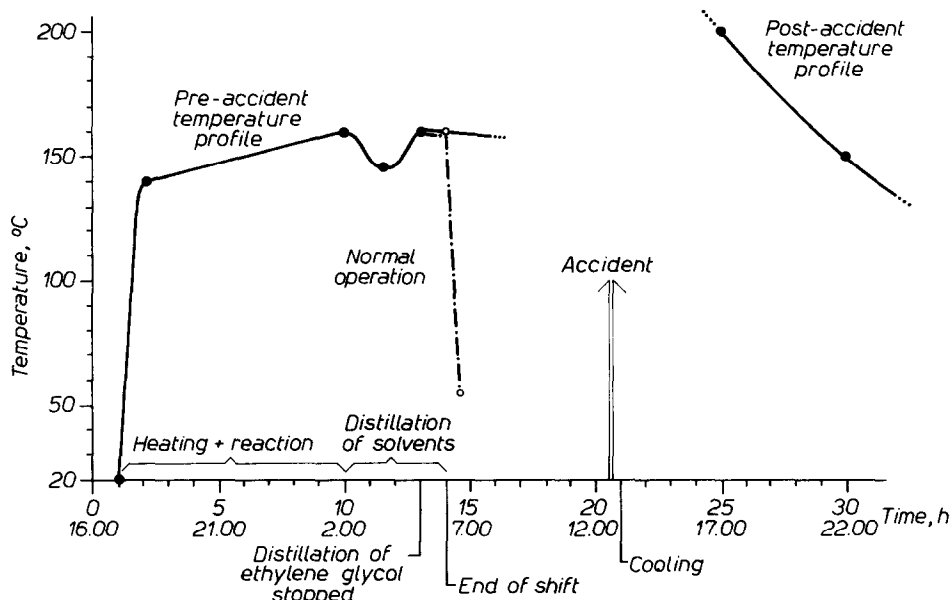


Fig. 1. Temperature profile during operation and after the accident [8, 9].

The above statement also turns out to be wrong from other papers and patents [30–32] in which the alkaline hydrolysis of 1,2,4,5-tetrachlorobenzene was carried out with the above-mentioned ratio definitely lower than 5 without any mention of uncontrollable exothermic reactions. Besides, the Seveso accident took place *after* the hydrolysis. In addition to that, the vast majority of patents claims temperatures of over  $200^{\circ}\text{C}$  for the production of TCP, without mentioning uncontrollable exothermic reactions [31–40].

The accident at Coalite in Great Britain in 1968 in a plant using the process with ethylene glycol as reaction medium was caused by an uncontrollable exothermic reaction starting at  $225\text{--}230^{\circ}\text{C}$  [26, 41]. In this accident [41] the above temperature was reached due to heating from outside, very probably following a breakdown of the reactor's oil heating circuit [5].

The other accidents concerning the methanol process (they will be examined later) do not give any information useful to obtain an understanding of the Seveso accident. Therefore, on the ground of what was known before

July 1976 it was not possible to point out either the causes, or the dynamics of the accident. Even the hypothesis of a possible exothermic reaction occurring inside the reaction mixture because of the presence of air must be rejected according to some experiments carried out to this purpose [20–22], and in particular to those experiments concerning the ethylene glycol–NaOH–air or –nitrogen systems [42].

To understand what has happened in the ICMESA reactor it was therefore necessary to determine the behaviour of both the mixture and its components connected with TCP production under different conditions.

### Thermal stability of the “Seveso mixture”

Several authors studied the thermal stability of the mixture and its components supposedly present in the reactor. All available methods of thermal analysis were used: simultaneous thermogravimetry and differential scanning calorimetry (TGA/DSC) [20, 21], differential thermal analysis (DTA) [22], miniautoclave (Thermische Zersetzungsprüfung, TZP), Sikarex, Dewar flask [23], accelerating rate calorimeter (ARC) [24] under different experimental conditions (dynamic, isothermal, adiabatic, isochoric, and isobaric); in open platinum sample holder, in air or nitrogen; in closed crucibles of nimonic, glass or gold.

The most significant results of these studies can be summarized as follows:

- The atmosphere surrounding the sample and the material of the container does not affect the observed exothermic behaviour.
- The “Seveso mixture” kept at 160°C does not show appreciable exothermic reactions.
- The experiments in miniautoclave (TZP) do not show exothermic reactions below 200°C; self-heating of the mixture proceeds at an appreciable rate only above this temperature [23].
- DSC measurements with an instrument made in 1970 did not show any exothermic behaviour below 230°C [20].
- DSC/DTA measurements with more recent instruments show — both under dynamic and isothermal conditions — slow and weak (about 105–125 J/g) exothermic behaviour starting at 180°C; these phenomena were previously unknown. These measurements also show other, known and more intense exothermic reactions above 230°C [20–22] (Figs. 2 and 3).
- In the Sikarex calorimeter, under isothermal conditions and with open sample holder, the self-heating proceeds at an appreciable rate only above 200°C; under adiabatic conditions, with open sample holder at 160°C, the temperature of the mixture increases by about 10°C in four days; at 180°C only a small temperature gradient can be observed, which gets exhausted after 24 hours [23].
- Under heat-accumulating conditions (Dewar flask) at 180°C the temperature increases by 1–2°C only, and the rate of pressure rise is 10 mbar/h [23].

- The adiabatic calorimeter ARC confirmed existence of a first exothermic effect at 180°C ( $\Delta H$  122 J/g), strong enough to increase the temperature by about 60°C (under strictly adiabatic conditions) and to start a second, more violent, runaway reaction. The ARC test also showed that, above

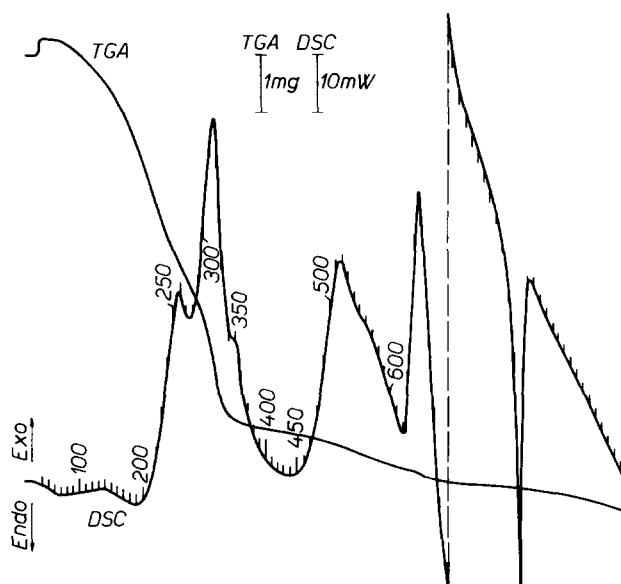


Fig. 2. Simultaneous TGA/DSC (Thermaxanalyzer Mettler TA 2000 C): sample 9.8 mg; heating rate 25°C/min; nitrogen flow 60 mL/min [20, 21].

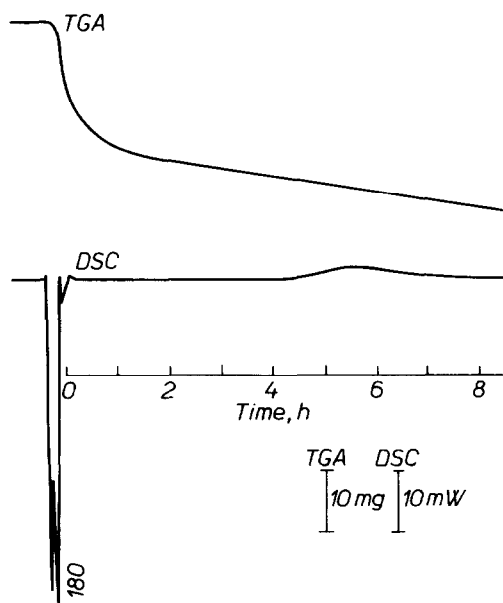


Fig. 3. Simultaneous TGA/DSC: sample 56.7 mg; isothermal temperature 180°C; nitrogen flow 60 mL/min [20, 21].

180°C, the mixture gets self-heated, always in adiabatic conditions, causing a pressure increase of 4 bar (the safety disk at ICMESA was set at this value) in 8 hours [24] (Figs. 4–6).

However, these results do not explain how the content of the reactor (or at least a part of it) could be overheated from 158 to 180°C, the minimum temperature necessary to start the weak and slow exothermic reaction described before. In fact, it must be remembered that the ICMESA reactor was connected with the atmosphere through large capacity condensers, and that the mixture contained in the reactor was undergoing evaporation; therefore the conditions were far from adiabatic.

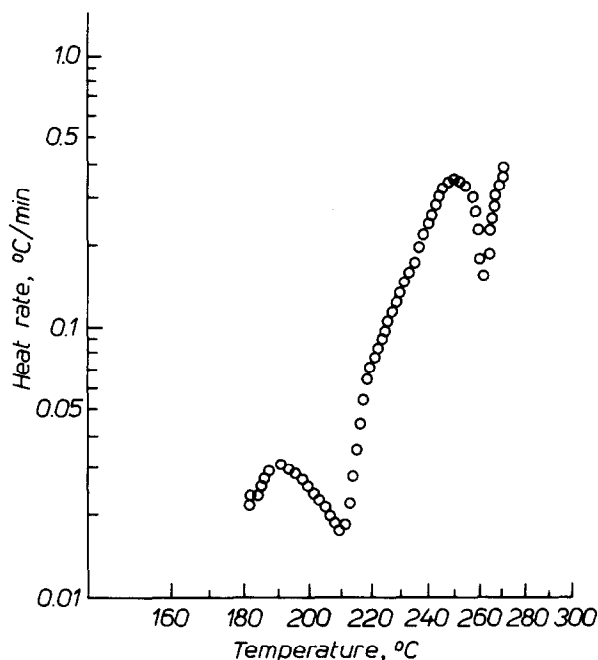


Fig. 4. Accelerating rate calorimeter (Columbia Scientific Industries): heat rate vs. temperature: sample 3.12 g; Hastelloy C bomb;  $\phi$  factor 1.94 [24].

It follows that the Seveso accident can be explained only by admitting that:

- (1) in the first stage at least an appreciable part of the mixture had been heated by an external source from 158 to 180°C;
- (2) the weak and slow exothermic processes seen before started at this temperature;
- (3) the heat generated during this reaction, added to heat coming from the external source, increased the temperature up to 200°C and even more. At about 230°C, the previously known exothermic reactions which caused the rupture of the bursting disk must have occurred.

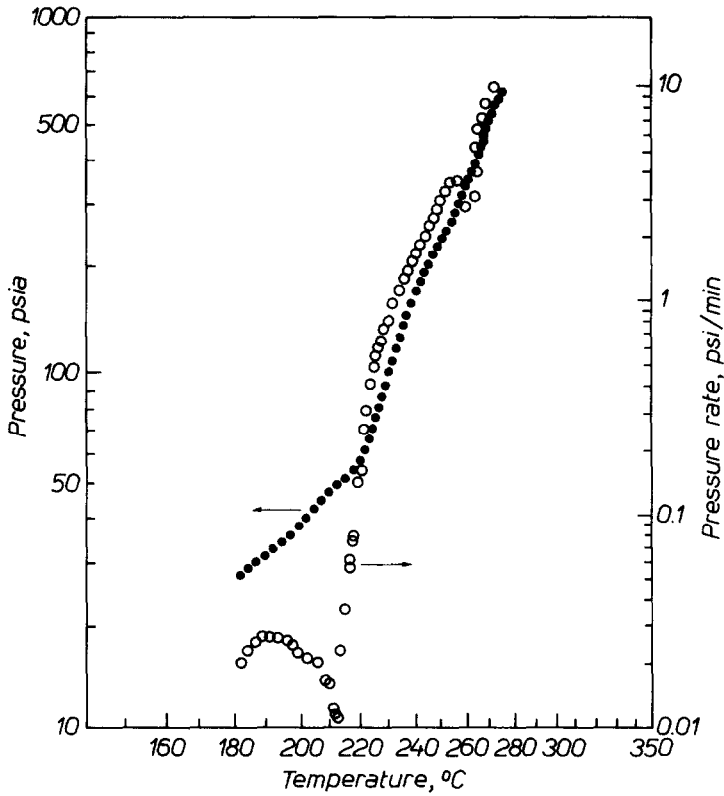


Fig. 5. Accelerating rate calorimeter: pressure and pressure rate vs. temperature [24].

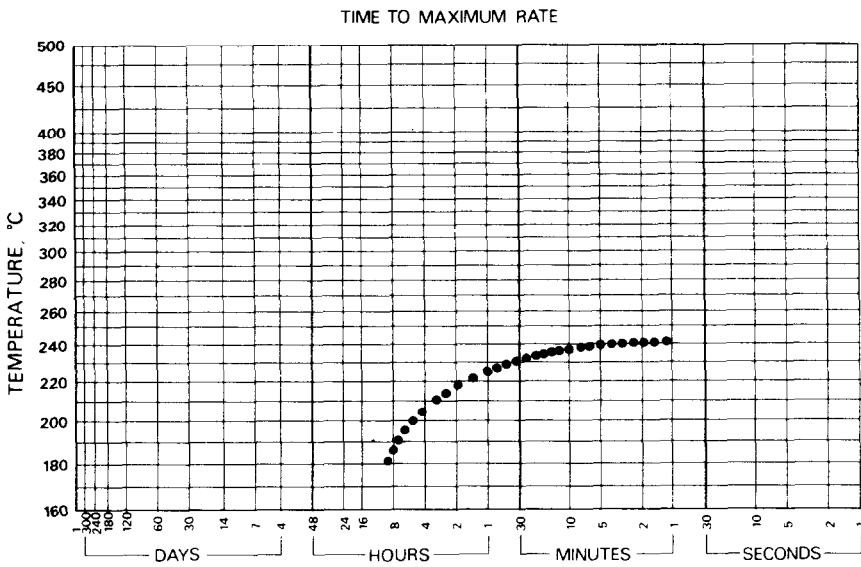


Fig. 6. Accelerating rate calorimeter: time to maximum rate vs. temperature [24].

## The research of Theofanous and its implications

As at the interruption of the operations the steam to the reactor had been stopped too, the reactor was no more under influence of external heating. The only source of heat which may have initially heated at least an appreciable part of the mixture from 158 to 180°C had therefore to be located in the dry wall of the reactor, which was at about 300°C. However, the quantity of heat concentrated in this part of the wall was relatively small, and could not heat the liquid in the reactor more than 2–3°C. It can be expected that this heat would partly disperse and partly distribute along the whole wet wall and from there to the liquid without increasing significantly the temperature of the bulk of the mixture in the reactor; certainly this increase could not heat an appreciable part of the reactor content up to 180°C [6].

Only Theofanous' research, at first theoretical and later experimental, makes it possible to explain what happened in the ICMESA reactor.

Briefly, he experimentally investigated heat transmission from a steel slab partly submerged in water held in a vessel in the shape of a parallelepiped, only the dry part of the slab being heated electrically [17]. Then he tested the same phenomena in a reactor similar to that used in Seveso (Seveso/model reactor diameter ratio 3.15), containing ethylene glycol. The upper dry wall of the experimental reactor was also heated electrically [18].

The experimental results were used to simulate the behaviour of the Seveso reactor during both the initial heat-up from 158 to 190°C and the following temperature increase to about 230°C, all taking into account the kinetics of the chemical phenomena — beginning from 180°C — which must have had influence upon at least part of the reactor content [18].

Theofanous demonstrated that — in contrast with what would be expected — the heat, accumulated in the emerging part of a steel slab submerged into a quiet liquid in a vessel, is transmitted to the upper layer of the liquid. This is valid generally, i.e., for different liquids and over a wide range of temperatures.

In the Seveso reactor, the small amount of heat accumulated in the dry wall of the reactor during heating by the superheated steam, would have uniformly heated an upper layer of a few centimeters of the liquid, raising the temperature of this layer from 158 to 180–190°C in about 10 minutes.

At this temperature the slow exothermic reaction (discussed before) started, causing another source of heating in addition to the heating caused by the previous reaction which would have continued. As a consequence, in about 7 hours the surface of the liquid in the reactor reached a temperature of about 230°C while the temperature of the rest of the reactor contents remained at about 158°C (Fig. 7). At 230°C the known, strongly exothermic reaction caused the rupture of the bursting disk, although the reactor was connected with the atmosphere through a pipe (Fig. 8). The reaction involved the whole contents of the reactor in a short moment.



Among the several conclusions reached by Theofanous it may be remembered that:

- The Seveso accident occurred under really marginal conditions: minor variations in the initial conditions (time of stirring, amount of ethylene glycol distilled) could have been enough to avoid the accident.
- The "Seveso mixture" as contained in the ICMESA reactor could not cause a violent reaction to occur even if initially heated to 210°C;

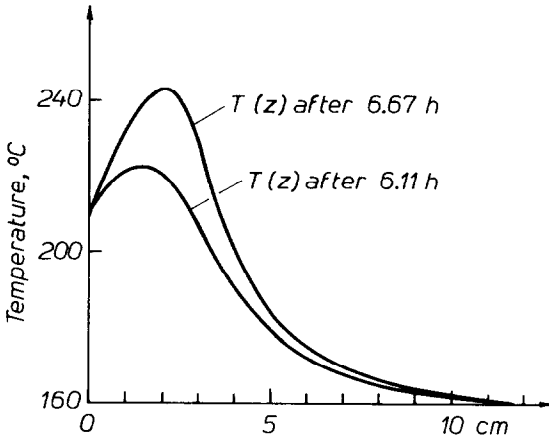


Fig. 7. Thermal profile in the liquid vs. depth from the surface after different times. Adapted from Ref. [18].

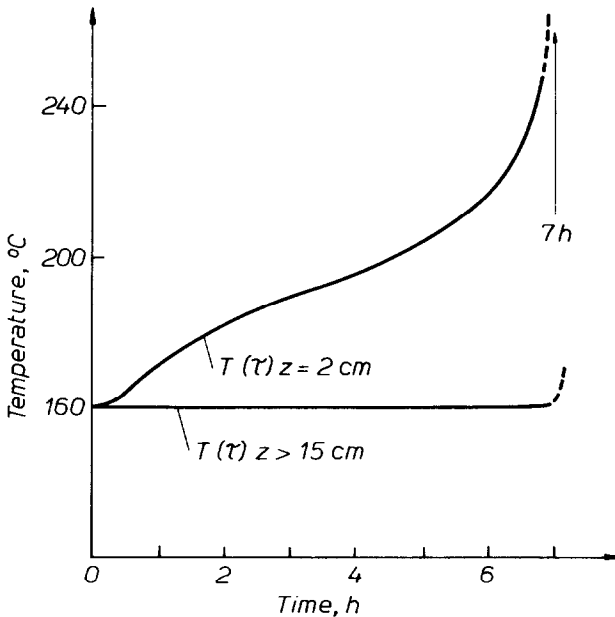


Fig. 8. Thermal profiles in the liquid vs. time since the operations stopped, at two different depths from the surface. Adapted from Ref. [18].

- The accident can be explained only by admitting that more ethylene glycol had been distilled than has been declared by the operators.

This conclusion is in agreement with that published by Mazza, Scatturin and others [43] and with the ARC data [24].

As regards the safety and control systems, Theofanous' results show that an alarm system connected with the thermometer (certainly well-immersed in the liquid mass, as usual in these cases, and taking into account the variation of the liquid level during the operation) would not have been able to ensure intervention at the right time. In fact, the temperature of the reacting mixture, with the exception of the upper layer, maintained its initial value of 158°C — or was maybe a little lower than that — practically until the instant of the rupture of the disk.

Theofanous' studies show that the runaway phase of the Seveso accident was sudden and not even an alarm system based on pressure relief inside the reactor would have been effective, considering that the reactor was connected with the atmosphere.

### Safety criteria in TCP production

The safety criteria to observe in TCP production depend basically on the following elements:

- thermal stability of the reactant
- physico-chemical characteristics of the alkaline hydrolysis of tetrachlorobenzene
- operating conditions (type of process, system of heating, etc.)
- possibility of particularly toxic by-product formation (2,3,7,8-TCDD)

As regards the first point, today's knowledge allows a confirmation that runaway reactions can occur at a temperature of around 230°C. For a reasonable safety margin it is better not to let temperature exceed 180°C. Furthermore, up to this temperature the concentration of 2,3,7,8-TCDD formed as by-product is low enough not to present particular risks [26, 44]. The maximum temperature of 180°C is therefore recommended also to keep the formation of particularly toxic by-products at a negligible level.

The most delicate step of the whole TCP production process is the tetrachlorobenzene hydrolysis, because of its exothermal nature. However, it should be observed that, regarding safety, different situations could happen according to the kind of reaction medium used; in an industrial process, the medium is either methanol or ethylene glycol.

Considering the temperature needed for the reaction, the vast majority of the patents quote temperatures of 180–200°C or even higher, but operation at 140–160°C is possible. Methanol processes must be operated under pressure, while ethylene glycol processes can be carried out at atmospheric pressure in an open system.

It follows that in the case of methanol batch processes operated in a closed system, the alkaline hydrolysis of tetrachlorobenzene is influenced by

spontaneous increases in temperature and pressure. On the contrary, in the ethylene glycol processes carried out in an open system, reaction temperature can be controlled by the continuous evaporation of reaction water.

During the exothermic stage of alkaline hydrolysis of tetrachlorobenzene in the methanol process, the maximum temperature attainable depends on the ratio methanol/tetrachlorobenzene and, in particular, on the temperature at which the reaction starts and on the more or less complete dissolution of NaOH (always used in excess).

In ARC experiments [45] carried out under the conditions quoted in a patent [27], we observed that during the alkaline hydrolysis of tetrachlorobenzene in methanol the temperature can spontaneously exceed 230°C. At this temperature a runaway reaction occurs. Also, the recently revealed, weak and slow exothermic reaction [20, 22] can help the reaching of this critical level. To face this situation it is essential to provide plants using the methanol process with adequate control systems, in particular to avoid exceeding a temperature of about 200°C during the alkaline hydrolysis of tetrachlorobenzene.

In the ethylene glycol process, difficulties may arise during the tetrachlorobenzene hydrolysis in case of line clogging, which would cause cessation of operation in an open system at a self-regulated temperature. These cloggings may be caused by tetrachlorobenzene sublimation; therefore this phenomenon must be minimized by choosing a low reaction temperature, for instance 150–160°C. In any case, the lines susceptible to clogging should have a diameter large enough to avoid this possibility. Besides, during hydrolysis, the process must be strictly monitored and the reactor should have an efficient cooling system to be able to manage emergency situations.

As concerning safety, there are also differences between methanol and ethylene glycol processes in the solvent distillation step. In the methanol process, at the end of the hydrolysis the reaction mixture contains, besides sodium trichlorophenate and NaCl, the reaction water, the by-product (dimethyl ether), formed by methanol condensation, and methanol itself. The distillation of the latter may be complicated by the presence of dimethyl ether — a gaseous compound, b.p. -23.5°C, easily inflammable — and particularly by the fact that at the end of the distillation the trichlorophenate obtained is practically dry, with the possibility of dangerous local overheating. In the ethylene glycol process, on the contrary, the by-product formed by the ethylene glycol condensation is diethylene glycol — a high-boiling compound, b.p. 244.5°C — which is not removed during the distillation of monoethylene glycol. Therefore, this is constantly present with the trichlorophenate, and risks of overheating are avoided.

Finally, the heating fluid used in the different steps of the process is important. The most suitable is steam at a pressure of, for instance, 11–12 bar, to avoid in any case the temperature of the liquid mixture exceeding 170–180°C. Considering the phenomena illustrated by Theofanous, this steam should be just a few degrees superheated, to avoid anomalous local

overheating in the non-stirred mixture. In addition, in case of use of superheated steam at higher temperature, besides the usual pressure gaging on the steam line, temperature must be controlled as well.

Should an oil heating system be used at a temperature notably above 200°C, adequate control systems must be arranged in such a way as to avoid in the event of a heating system breakdown the temperature of the reactor content approaching the maximum oil temperature. This solution was chosen, for example, after the 1968 accident in the new Coalite plant [41].

The knowledge of the behaviour of the different substances — including by-products — and of the mixtures used in a chemical process, and a critical examination of the operating conditions allows a much more efficient definition of safety criteria than those that could be called *a posteriori*. In this case, it would not be necessary to employ safety devices, which are sometimes extremely complex and not always safe and reliable. This consideration is in particular directed to the blow-down systems for the rapid containment of possible effluents.

In TCP production via the ethylene glycol process, the implementation of the criteria exposed here guarantees that toxic substances cannot escape from the reactor, thereby avoiding the use of the debated blow-down systems [11]. In fact, these systems are calculated and used for particular operations in the chemical industry when the parameters for the calculation (in particular: quantity and volume of effluents and dynamics of the process) are known or foreseeable.

Specialists in this field still meet with difficulties in designing these systems, even when several elements for the calculation are available [7, 46]. These difficulties involve, in some cases, also the calculation of the bursting disks [47]. For this reason an institute specialized on this matter (DIERS) was founded in the USA in 1976 [1, 47, 48].

On the other side, it is also well known that miscalculation of blow-down systems may have serious consequences [47, 49]. The realization of these systems cannot be improvised and, in the event of a lack of data allowing reliable execution of a project, it is better to face safety problems in another way. First of all a thorough knowledge of chemical systems is necessary, attaining to what was defined as preventive safety.

## Conclusions

The causes and the dynamics of the Seveso accident have been clarified by Theofanous and others: the accident was caused by unexpected concentration of a quantity of heat, moderate indeed, in the upper layer of the unstirred liquid in the reactor. The temperature of this upper layer reached a level at which slow and weak exothermic processes, previously unknown, started. After about 7 hours these processes contributed to the start (always in the upper layer, at about 230°C) of other and more rapid, exothermic processes, which caused the rupture of the bursting disk. Immediately after

that a large part — if not all — of the mass was affected by these processes.

The comparative analysis of 2,4,5-trichlorophenol production processes allows proposition of an acceptable explanation of previous accidents at other plants too. This analysis shows that plants where methanol is used as the reaction medium are characterized by an intrinsic risk, both during the tetrachlorobenzene alkaline hydrolysis and during the distillation of the solvent. This is not the case when ethylene glycol is the reaction medium.

The recently achieved knowledge on the thermal stability of the substances and mixtures used in the production of TCP also allows a definition of design criteria assuring safe operation conditions for the ethylene glycol process.

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