

POST INVESTIGATION OF AN INCIDENT DUE TO THE SELF-POLIMERISATION OF A COMMERCIAL MONOMER

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In the last decade, the importance of risk analysis in the transport of dangerous goods has been evidenced by several studies showing that in some cases the risk associated with the transport of hazardous substances can be compared to those in chemical plants (processing units and storage).

In this work the analysis of an accident in transport of dangerous goods is described. The objective of this study is to contribute to the determination of the causes that brought about the self-polymerization of commercial divinylbenzene (DVB 63%) contained in an isothermal-container, in order to prevent future occurrence of this type of accidents.

Residence time and conditions during transport and storage of monomers, in particular the storage temperature, are very important factors that affect their self-polymerization aptitude. Concerning the cause of accidents it has been supposed that the quantity of oxygen in the tanker probably was insufficient to activate properly the inhibition mechanism to prevent the self-polymerization. According to this consideration the self-polymerization of DVB and the inhibition mechanism of 4-tert-Butylcatechol (TBC) have been studied as a function of temperature and monomer exposure to air with Differential Scanning Calorimetry and Adiabatic Calorimetry.

1. INTRODUCTION

During the past decade several studies have demonstrated that incidents related to the transportation of dangerous goods are comparable in number and magnitude to those occurring in chemical plants. This is evident considering that tankers for the transport of dangerous substances, even containing a smaller quantity than storage tanks, often crosses urban areas with high population density, Egidi et al. (1995), Leonelli et al. (1999), Bubbico et al. (2006), Milazzo et al. (2002) and Milazzo et al. (2010). According to these considerations, it is obvious that the transport of dangerous substances can cause severe risk to human health and environment. For this reason, even without a specific legislation to control the risk associated with the transport of hazardous goods, methods and risk analysis tools have to be used in order to estimate risk indexes.

This paper focuses on an incident in the transport of divinylbenzene. The objective of this work is to contribute to the determination of the self-polymerization causes. The event has been examined from the experimental point of view and then a consequence analysis has also executed. In particular it has been investigated the hypothesis of the insufficient quantity of oxygen in the tanker to properly activate the inhibition mechanism. According to this consideration the influence of the exposure to air on the self-polymerization of the monomer and on the inhibition mechanism have been studied. To this purpose different calorimetric techniques have been applied, in particular the Differential Scanning Calorimetry and the Adiabatic Calorimetry. Then a simulation of the event has been performed by means of mathematical models. Data processing has provided a risk index, which allows

drawing a risk map. Results point out the need of a detailed analysis of all potential scenarios associated to the transport of the substance in order to manage the emergency.

2. THE INCIDENT

Divinylbenzene (DVB) is an aromatic monomer used principally for cross-linking styrene in the production of ion exchange resins. Much of this production is located in Europe. The 23rd August 2006, in the Scottish seaport of Grangemouth, 24000 liters of DVB 63% contained in a tanker exposed to sunlight on the docks self-polymerized. The tank fracture, due to its displacement, caused the loss of very big amount of DVB, as white and dense plume of vapours. The firemen sealed off the zone for a range of 500 meters. The residents were not evacuated but they were forced to stay home for 24 hours as a preventive measure because of the irritating characteristics for the skin and eyes of the substance. The seaport was idle for 36 hours, until the wind had completely dispersed the cloud of vapours. No injuries were reported. Figure 1 shows the location of the incident (a) with the sealed off zone (b).

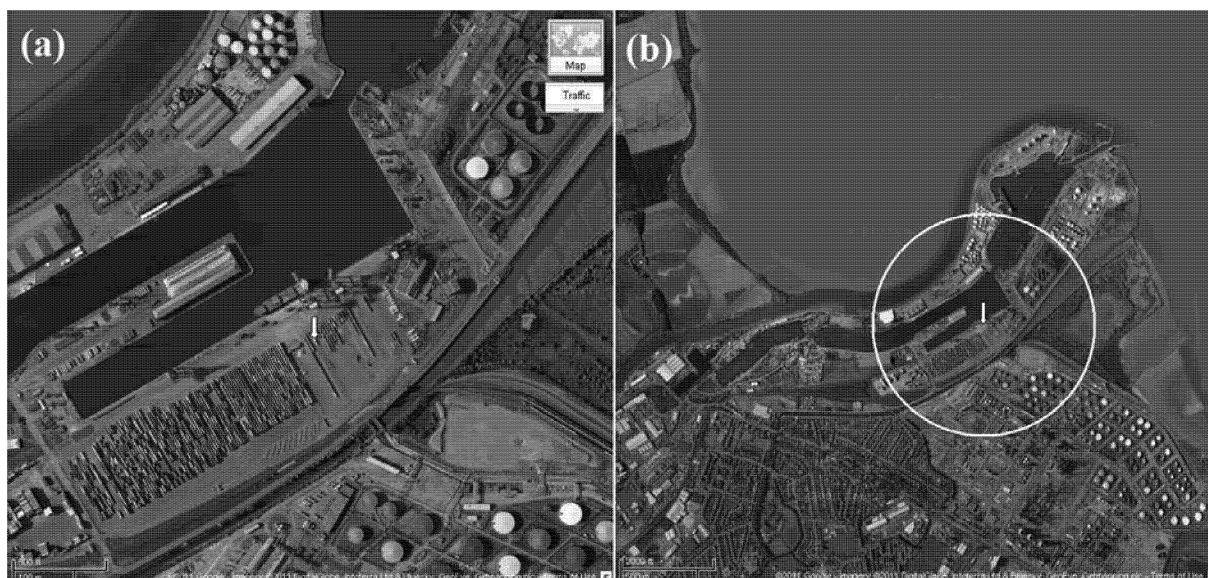


Fig. 1. Emergency zone (the ray of the circle is equal to 500 m).

Divinylbenzene is a flammable and toxic liquid and is stored in atmospheric tankers. According to its properties, the common equipment design and handling techniques for its hazardous class must be practiced to prevent conditions that can cause fire or explosion and/or the dispersion in the air. To stabilize this monomer, usually 4-tert-Butylcatechol (TBC) is added at a level of 900-1200 ppm by weight to act as an inhibitor to prevent the self-initiated self-polymerization of the material. From available data, it is known that oxygen influences considerably the inhibition properties of TBC. For this reason, in this study attention has been paid to the effect of atmospheric oxygen exposure of DVB/TBC system and to the storage temperature.

3. OXYGEN ROLE IN INHIBITION MECHANISM

DVB polymerizes by a self-initiated radical chain mechanism. Termination can be either by the reaction of two polymer radicals (by combination or by disproportion, Bowden 1969) or by the action of the inhibitor. Self-heating will be due to the exothermic polymer radical propagation. The inhibition mechanism of TBC toward

DVB is highly influenced by oxygen. It has been reported by Morrison et. al. in 1997 that the TBC radical can also react with oxygen, probably with the formation of a TBC peroxy radical, which could itself form a peroxide either by reaction with a polymer radical or with a TBC radical:



The new radical, depending on its reactivity may either terminate another radical or initiate polymerization either by addition of a monomer or by chain transfer to a monomer. There may also be homolysis of the peroxide O-O bond with the production of two radicals $\text{PO}_2\cdot$. These radicals may then react by terminating radicals or by acting as initiators for polymerization. At lower temperatures the peroxides would be expected to react more by chain transfer and the radical produced to terminate another radical. At higher temperatures homolysis of the O-O bond would be expected to predominate and the radicals formed to initiate polymerization. The peroxides may therefore pass from having an inhibiting effect at low temperatures to acting as initiators at higher temperatures. Because of the possible reaction of the TBC radical with oxygen there may not be an exact stoichiometric ratio between oxygen and TBC consumed. Oxygen is present dissolved in the DVB and in the air in the container head space. The molar ratio (R) of available oxygen to TBC is an important factor in TBC inhibition. A concentration of 15 mg/l has been reported for oxygen dissolved in DVB at 25°C. For a TBC concentration of 1200 ppm R is ≈ 0.06 . So the inhibition mechanism discussed requires the formation of radicals. Considering just the first two steps of inhibition mechanism, as inhibition takes place during the early part of the reaction, the contribution from the termination may be neglected. The two important differential equations then become

$$\frac{d[\text{P}\cdot]}{dt} = v_1 - k_f[\text{P}\cdot][\text{O}_2] + k_r[\text{PO}_2\cdot] \quad (2)$$

$$\frac{d[\text{PO}_2\cdot]}{dt} = k_f[\text{P}\cdot][\text{O}_2] - (k_r + k[\text{TBC}])[\text{PO}_2\cdot] \quad (3)$$

with reaction rate constants k_f for the forward reaction and k_r for the reverse reaction of the first step and with a reaction rate constant k for the second.

Application of the steady state approximation to $\text{PO}_2\cdot$ gives

$$[\text{PO}_2\cdot] = \frac{k_f[\text{P}\cdot][\text{O}_2]}{(k_r + k[\text{TBC}])} \quad (4)$$

Substitution into Eqn, (2) gives

$$\frac{d[\text{P}\cdot]}{dt} = v_1 - \frac{k_f k[\text{P}\cdot][\text{O}_2][\text{TBC}]}{(k_r + k[\text{TBC}])} \quad (5)$$

Two situations may be considered

Case (a) $k[\text{TBC}] \gg k_r$

$$\frac{d[\text{P}\cdot]}{dt} = v_1 - k_f[\text{P}\cdot][\text{O}_2] \quad (6)$$

Case (b) $k_r \gg k[\text{TBC}]$

$$\frac{d[\text{P}\cdot]}{dt} = v_i - \frac{k_f k[\text{P}\cdot][\text{O}_2][\text{TBC}]}{k_r} \quad (7)$$

Remembering that the equilibrium constant for the formation of $[\text{PO}_2\cdot]$ is

$$K = \frac{k_f}{k_r} \quad (8)$$

$$\frac{d[\text{P}\cdot]}{dt} = v_i - kK[\text{P}\cdot][\text{O}_2][\text{TBC}] \quad (9)$$

In case (a) soon after a $\text{PO}_2\cdot$ radical is formed it is removed by reaction with TBC. This would correspond closely to the usual view of an inhibitor if oxygen was regarded as the inhibitor. In case (b) there is the possibility of some build up of $\text{PO}_2\cdot$ radicals. Both Eqns (6) and (9) show that the rate of inhibition depends on the concentration of oxygen dissolved in the DVB. In a container with no head space, inhibition will cease shortly before all the oxygen is consumed, meaning that only a fraction of ≈ 0.06 of the TBC has reacted. In a container with air in the head space a situation may be reached where the rate of inhibition becomes controlled by the rate at which oxygen is dissolving. After the reaction has started the inhibition reaction may go on but at an ever decreasing rate, and this would be manifested in an apparent self-acceleration of the reaction.

4. EXPERIMENTAL RESULTS

The aims of the laboratory tests are the comprehension of the role of the storage temperature in the auto-polymerization of DVB and of the role of the oxygen in the TBC inhibition mechanism toward this monomer, in order to validate the hypothesis done. The experimental runs here described have been carried out in a Differential Scanning Calorimeter (DSC): both isothermal (in order to evaluate the heat produced by the polymerization, the conversion and the induction period as a function of the set temperature) and scanning tests ($5^\circ\text{C}/\text{min}$ from 30°C to 250°C , whose objective is to determine the onset temperature of the reaction) have been run. In all DSC tests a mass of $20\ \mu\text{g}$ of DVB at room temperature has been processed in aluminium pressured pans. The results of the first scanning test on fresh DVB is a detected onset temperature of 162°C and the maximum value of the temperature of 173.7°C . In figure 2 the heat fluxes evolved during the polymerization are reported for all the isothermal tests done. It is possible to observe that the reaction rate increases and the induction period decreases when the set temperature changes from 110°C to 140°C : in the first experiment the temperature peak is reached after 175 minutes from test beginning and it gradually slides to 10 minutes in the last isothermal run. Incrementing the set temperature, also the height and the shape of the temperature peaks change: they become higher and sharper, indicating a more hazardous behaviour of the monomer at higher temperatures. The heat evolved by the polymerization also increases with temperature; it could be due to:

- At lower temperatures the viscosity of the reacting mass increases, so the final conversion decreases (because of the reduced mobility of the propagating chains) leading to a reduction of the total heat evolved.

- During the induction period, for tests run at temperatures below 140 °C, in presence of air and peroxides, DVB can be oxidized to epoxides (Morrison et. Alt., 1997), which are less reactive toward polymerization.

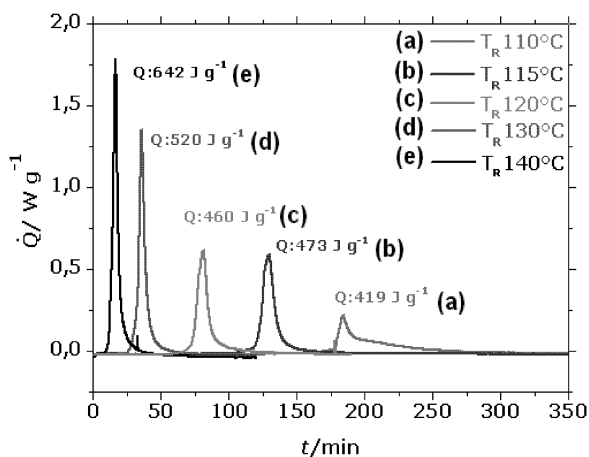


Fig. 2. DSC isothermal tests: the effect of temperature on auto-polymerization of DVB.

In order to determine the oxygen influence on TBC inhibition mechanism, a sample of DVB has been stirred (500 rpm, 50°C) for different periods, ranging from 0 to 13 days, in order to create a deep contact between the sample and the air. This modified sample has been tested in both scanning and isothermal experiments. In figure 3 the results of the scanning tests (5°C/min from 30°C to 250°C) are reported, where the 0d curve refers to fresh DVB. From this graph it's possible to see that incrementing the contact period between air (oxygen) and DVB/TBC system, the polymerization starts at higher temperatures. A considerable difference can be observed after 1 week of air exposure: in particular the curve that refers to an air exposure of 13 days shows that the onset temperature changes from 162°C to 178 °C.

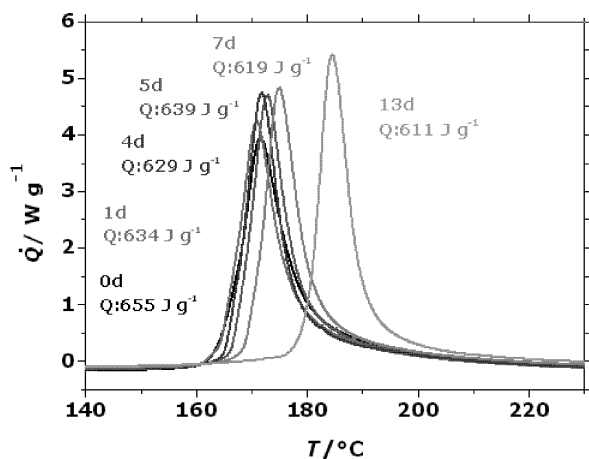


Fig. 3. DSC scanning tests (5°C/min): the effect of air exposure on DVB polymerization.

Experimental profiles derived from isothermal tests (set temperature: 130°C) are shown in fig. 4. The 0d curve refers to fresh DVB, and the other to treated DVB as explained before, for 1 to 7 days.

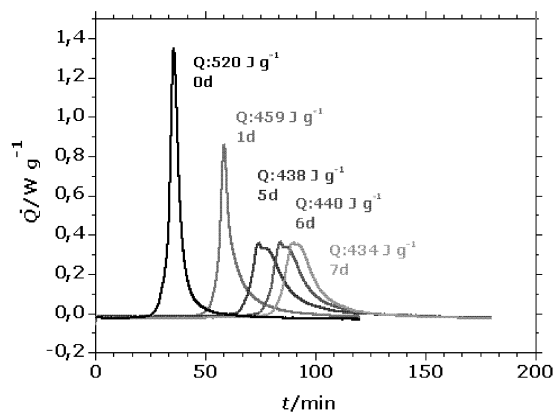


Fig. 4. DSC 130°C isothermal tests: the effect air exposure on DVB polymerization.

These data show that induction period increases for longer air exposures, confirming the role of the oxygen in TBC inhibition mechanism. Passing from shorter to longer air exposures also the shape of the peaks changes, getting lower and rounded, and the heat evolved by the reaction decreases: these facts sustain the hypothesis of the DVB oxidation to epoxide. So oxygen carries out two actions in this process: it promotes TBC inhibition mechanism incrementing induction period but it also oxidize DVB, making the monomer inactive to polymerization (deduced by a lower heat evolved during reaction and a lower reaction rate).

To validate the results just explained, adiabatic tests have in different chemical atmospheres have also been run. Results are briefly shown in table 1.

Table 1: Adiabatic tests: comparison between air and nitrogen atmosphere.

DVB [g]	atmosphere	Tonset [°C]	Tmax [°C]	ΔTad [°C]	Pmax [bar]
50.38	air	103.5	397.9	294.4	8.8
50.35	N2	87.7	394.5	306.0	7.4

In figure 5 the experimental profiles of temperature and pressure versus time are shown for the air pressurized test.

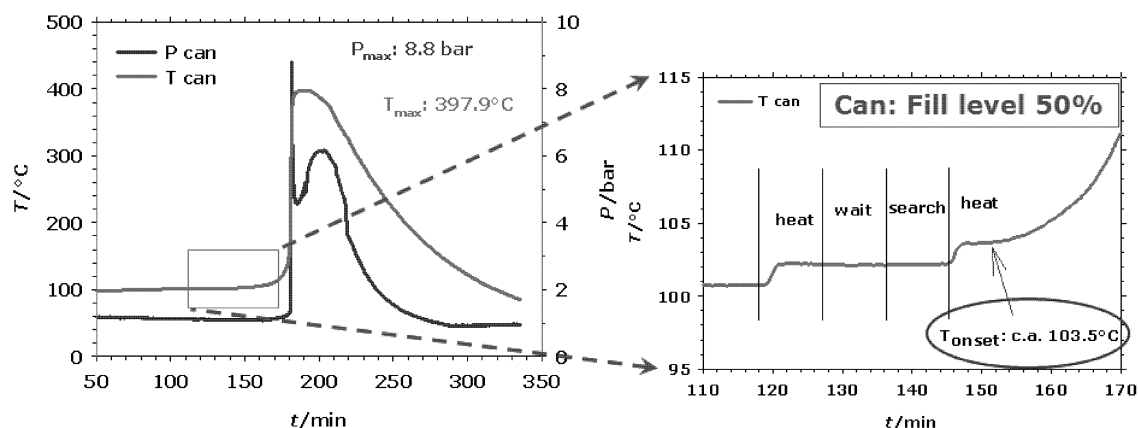


Fig. 5. Adiabatic test of DVB in air.

These experimental data confirm the importance of oxygen in TBC inhibition mechanism: in fact the runaway behavior of the monomer is stronger in presence of nitrogen than in air. The detected onset temperature decreases of 16°C from air to nitrogen condition test, while ΔT_{ad} increases of 11.6°C, as a prove of the inadequacy inhibition of TBC toward DVB in lack of oxygen.

5. POST-INCIDENTAL ANALYSIS

In the second part of the work the event has been modelled using specific simulation models. Firstly the event tree related to the release of the divinylbenzene has been constructed in order to identify the potential incidental scenarios. The event tree technique has also allowed the determination of the frequencies associated with each scenario. On the basis of knowledge of the storage conditions and the physical-chemical properties of the substance (Weast, 1985) the event tree of figure 6 has been obtained.

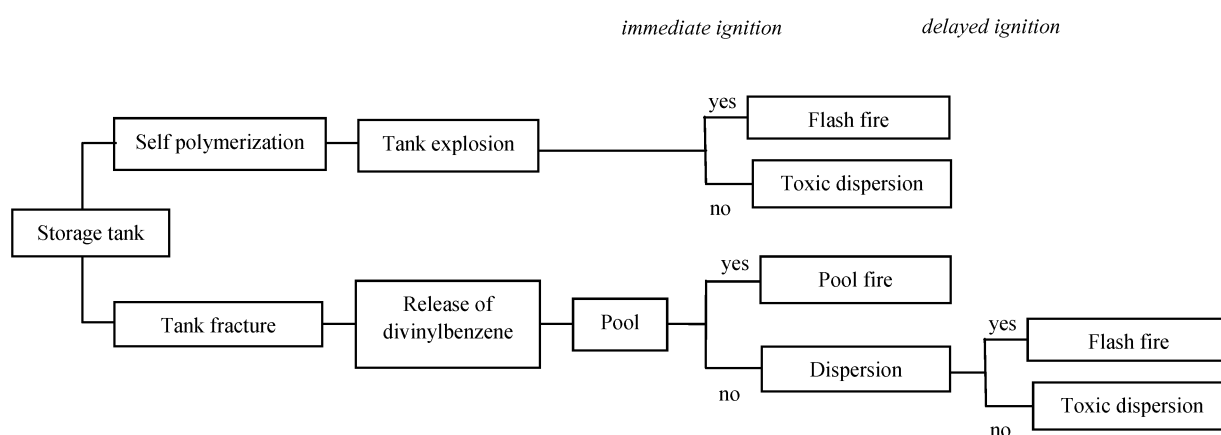


Fig. 6. Event tree.

According to the event tree, an explosion could occur following the self-polymerization, this is due to the exothermic reaction. In the case of the release of liquid, a pool is generated; if an immediate ignition occurs, a pool fire could be triggered. In absence of immediate ignition the substance evaporates and a toxic and flammable cloud diffuses in the atmosphere. The cloud could give a flash fire (or an explosion if the concentration of DVB is comprise in the explosiveness limits) or a dispersion of toxic vapours, depending on whether a delayed ignition will occur. In the case of the Grangemouth incident, the catastrophic explosion of the tank did not occur but, as confirmed by the experimental results, the heating of the mass due to the self polymerization caused the vaporization of a portion of monomer that was released in the atmosphere because of the fracture on the container due to its displacement. After the calculation of the amount of DVB in the cloud, the consequence estimation of the toxic dispersion has been executed using the mathematical models of the TNO (Yellow Book, 1997). Dispersions are affected by weather conditions, in this study the worst weather situations has been selected, named F2, which refer to the stability class F with wind speed of 2 m/s. Then, using Probit functions, the *probability of damage* has been calculated and expressed as a function of the *dose*, which represents the entity of the consequence of a certain scenario. Finally the risk index has been obtained by multiplying the probability of damage and the frequency of the release. Frequency data was available in the HSE report. Figure 7 shows the results of consequence assessment. Since immediate toxicity data of DVB are not available in literature, the iso-consequence curve has been drawn on the base of the TLV-TWA (threshold limit value -time weighted average). Using the TLV-TWA (10 ppm) the consequence evaluation is extremely conservative; however results show that the emergency area coincides with the area evacuated by firemen.



Fig. 7. Iso-consequence curve for the release of DVB (the ray of the circle is equal to 460 m).

The risk results have been shown using Cartesian graphs showing the dependence of the risk index (R , logarithmic scale) by the distance (d) from the point where the event is initiated. In figures 8 (a) and (b) the distance d represents, respectively, the downwind and crosswind directions. It is possible to note that the curves are not well defined near to the point of release due to the complexity of the consequence modelling in proximity to the source. The iso-risk mapping is shown in figure 9; the iso-risk curve has been drawn according to the most restrictive threshold limit of risk acceptability (10^{-8} event/year), defined by the TNO (CPS, 1999).

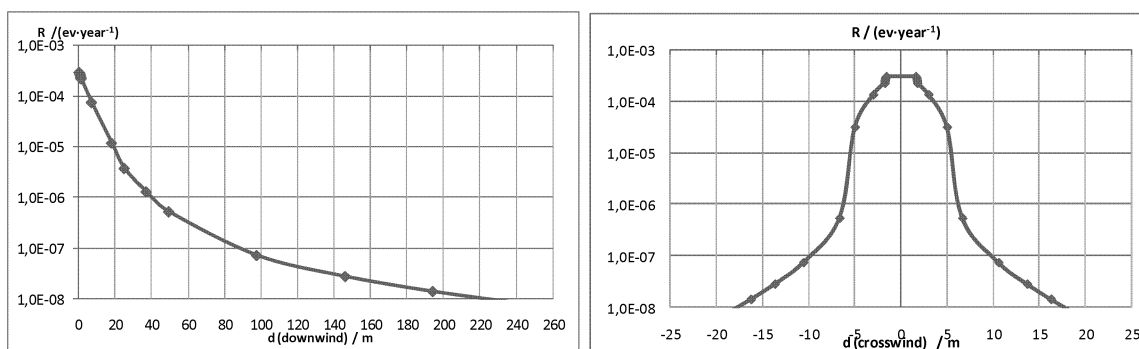


Fig. 8. (a) Risk vs. downwind distance for a toxic dispersion of divinylbenzene (meteorological condition F2); (b) Risk vs. crosswind distance for a toxic dispersion of divinylbenzene (meteorological condition F2).



Fig. 9. Iso-risk curve for the release of DVB (the ray of the circle is equal to 220 m).

The modelling provides results that in this paper are shown using two approaches: the consequence approach and the risk approach. The consequence approach (deterministic approach) is based on the evaluation of the extent of the incident without quantifying its likelihood. It is based on the identification of the worst scenario, thus if there are enough measures to protect the population from the worst incident, enough protection will also be provided for any incident. The iso-consequence curves are drawn by estimating the distance where the physical magnitude (describing the consequences) reaches a threshold value corresponding to the beginning of the undesired effect (fatality). The purpose of the risk approach (probabilistic approach) is not only to evaluate the severity of the potential incident, but also to estimate the likelihood of its occurrence. In general, the method uses more sophisticated tools and is more complete than the consequence approach. However, it is more complicated, time-consuming and expensive. It is based on the definition of a level of risk above which no person is permitted to be exposed. Concerning the incident examined in this paper, in figures 7 and 9 the circles corresponding, respectively, to the iso-consequence curve (for a concentration of 10 ppm) and the iso-risk contour (for a risk levels equal to 10^{-8}), are presented. The application of the consequence approach results in establishing a control zone of 460 m from the parking area of the tank, while the application of the risk approach results in a control zone of 220 m. There is a significant difference between the zones calculated by the two approaches.

Some considerations can be done about this observation. Applying the consequence approach, the worst scenario is associated to weather condition F2 (in the case of toxic dispersion). Taking into consideration the fact that in the D stability class is the most frequent, it is obvious anyway that this class is considered as relatively bad according to the consequence approach. Applying the risk approach, some uncertainties are introduced about the frequencies selected, but the protection must be increased for the stability class D because also the risk level increases due to the higher likelihood. This means that the extension of the zone delimited by the risk contour could be comparable with those delineated by the iso-consequence curve.

6. CONCLUSIONS

In conclusion, the aims of this paper are the comprehension of the role of the storage temperature in the auto-polymerization of DVB and of the role of the oxygen in the TBC inhibition mechanism toward this monomer, in order to validate the hypothesis done.

The shapes of the isothermal test DSC curves on fresh DVB can be explained using the mechanism for radical polymerization, self-acceleration phenomena are accounted for by the gel effect. The final conversion decreases as the reaction temperature decreases. This observation is important in order to estimate how much DVB was released to the atmosphere in the Grangemouth incident. As the polymerization proceeds the viscosity of the reacting system increases and this in some way must reduce the rate of initiation to such an extent that polymerization effectively ceases. The isothermal tests show that the final conversion varies approximately linearly with the reaction time and that the induction period varies logarithmically with the reaction time.

The quantity of dissolved oxygen is fundamental for the stability of the monomer.

Because of the low concentration of TBC and oxygen we must conclude that the probability of forming a peroxy radical in an encounter of a radical with an oxygen molecule is greater than that for a propagation reaction when a radical encounters a monomer.

The increase in the induction period for DVB stirred in presence of air must be due to an increase in the quantity of inhibitor and we must conclude that there is some partial oxidation reaction which is contributing to this.

The inhibiting effect of the oxygen on the auto polymerization reaction is evident by comparing the results with another adiabatic test carried out in a nitrogen atmosphere.

The simulation of the dispersion of the cloud of DVB has permitted a comparison between the consequence approach and the risk approach for the emergency management. Both the approaches can be used and provides useful information during the emergency situation.

7. REFERENCES

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