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# Development of a model for simulating the variability of the physical properties of substances, stored in various storage tanks, in the presence of an external heat source

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#### Abstract

In this paper a mathematical model for simulating the variability of the physical properties of substances stored in various storage devices (pressurised or cryogenic tanks etc.), in the presence of an external heat source, is presented. Design/construction characteristics including tank geometry, and all possible safety features (safety valves, liquid pump out, water deluge systems, water curtains, fire walls, external cooling by fixed or mobile fire fighting appliances) are taken into account in the model formulation. As an application example the case of an ammonia cryogenic storage tank is examined. In this example heat input arises from an adjacent storage tank being on fire and the time dependence of pressure and temperature of the tank and its content properties are calculated. The modular design of the model and the promising results allow the inclusion of the model developed in other more complicated packages (e.g. DOM-INO) in order to simulate accident evolution sequences in parallel with various operational interventions or additional safety features.

#### 1. Introduction

Anomalous occurrences in the process industries may be developed to major accidents with considerable impact to persons and/or environment outside the fence of the establishment. Major accidents such as in Flixborough, Seveso, Bhopal and Basel attracted public attention to safety of installations handling hazardous chemical substances. The demand for enhanced safety, accident prevention and mitigation of accident consequences challenges both plant operators and public authorities.

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Safety reviews of installations are effective for an early identification of hazardous situations that might arise and hence valuable for accident prevention purposes. However, very often consequences assessment becomes rather difficult, especially if domino type impact could aggravate the situation during accident evolution. Various models describing single undesirable events (release of flammable or toxic materials, dispersion of light or denser than air gases, pool/tank fires or jet fires, explosions – deflagration/detonation – with parallel generation of shock waves, missiles, etc.) are implemented in computer codes enabling consequence estimation [1].

Traditionally, water cooling rings and insulation have been used on storage tanks for avoiding ignition due to overheating from an adjacent tank/installation being on fire. A lot of experiments have been carried out in order to investigate the behaviour of storage tanks (mainly vessels containing LPG or propane) when they are engulfed in fire. The majority of these experiments included protected vessels or those equipped with water spray systems [2–13].

Fire protection regulations give general guide-lines on water application rates. There is however no theoretical description of the time dependence of the temperature and pressure of the contents of a tank exposed to heat radiation due to an adjacent tank being on fire. Increase of the cooling water application rate in order to better protect the tank may not always represent the best alternative. In fact additional environmental hazards may be created, since containment and environmentally acceptable disposal of used fire water becomes more difficult as its flowrate increases. Furthermore supply of huge quantities/flowrates of fire water can hardly be achieved with satisfactory reliability [2, 3]. On the other hand, studies for the effect of insulation on a storage tank refer to total engulfment of the tank by the fire, thus resulting in a homogeneous heat input by radiation [4, 5].

In this paper the development of a model which describes the time dependence of the physical properties of a storage tank exposed to heating from an adjacent burning tank is presented. Compared with other similar models [4, 5], in this model nonhomogeneous heat input has been considered. Also the influence of various parameters (tank size, spacing between tanks, filling height, existence of mitigation measures – cooling ring, water curtains, insulation – operational interventions such as liquid product pump out etc.) have been included in the formulation of the model. The effect of the view factor between the fire and the storage tank is also taken into consideration since it plays an important role for the calculation of the heat input to the storage tank. The model developed can be easily adjusted to describe other heat input sources to the storage tank such as total or partial engulfment or with simplification of the complicated phenomenon, jet fire impingement. It can also be adjusted to describe various types of storage facilities (atmospheric or pressurised storage). It has a modular form so as to be incorporated in larger programs/codes for consequence analysis (i.e. DOMINO).

In conclusion the model can be used to: (1) verify the adequacy of mitigating measures; (2) predict the time that a failure occurs; (3) provide information to be considered in risk analysis; (4) evaluate alternative protection/mitigation measures.

# 2. Physical formulation of the model

#### 2.1. Heat radiation from a fire to the storage tank

The initiating event is that a tank is on fire and the effect on adjacent tanks is to be studied. The shape of the fire is assumed to be cylindrical. The length, diameter as well as the effect of wind to the flames during burning are estimated using Thomas formulae [14, 15].

Heat from the fire to the tank is transmitted mainly by radiation (dominating mechanism). In order to calculate the heat radiation arriving on the target surface from the flame the following expressions are used:

$$Q_{\rm F} = \alpha \tau F Q_{\rm E}, \tag{1}$$

$$Q_{\rm E} = \varepsilon \sigma (T_{\rm f}^4 - T_{\rm amb}^4) \sim \varepsilon \sigma T_{\rm f}^4, \qquad (2)$$

where  $\alpha$  is the absorptivity of the target (~ 1);  $\tau$  is the atmospheric transmissivity; F is the view factor;  $Q_E$  is the emissive power of the fire.

In the equation for radiative heat transfer the view factor parameter plays a significant role. The view factor indicates the extent to which two objects can "see" each other and is given by the expression:

$$F = \int_{A_1 A_2} \int \frac{\cos \theta_1 \cos \theta_2}{\pi r^2} dA_1 dA_2,$$
(3)

where  $A_1$  is the surface of the target;  $A_2$  is the surface of the fire; r is the distance between the two elemental areas;  $\theta_1$ ,  $\theta_2$  are the angles made by the outward normals to the planes  $dA_1$ ,  $dA_2$  with the line joining the two elemental areas.

### 2.2. Heat exchange between storage tank and environment

Heat from the storage tank walls to the substance stored is transmitted by convection, conduction and eventually by radiation. Conduction is the heat transfer mechanism by which heat is transferred within the successive wall layers of the tank (e.g. for a cryogenic tank the external cover, the insulation and the steel wall). From all surfaces of the tank wall the dominating heat transmission mechanism to the contained liquid and vapour is convection while radiation is significant only when the temperature of the tank surfaces has increased a lot. Also heat is transferred from the tank walls to the contents of the tank by conduction. It must be noted that although this mechanism is not the dominating one, it cannot be ignored and it is more significant than radiation. In the described model all heat transfer mechanisms are taken in consideration for the estimation of the time variation of the physical properties of the wall of the storage tank and of the substance stored. In Table 1 the dominating heat transmission mechanisms for each part of the system are presented.

Different system parts	Heat input (dominating mechanism)	Heat output	
External layer of storage tank and cover	Radiation from fire (only to the part "seen" by the fire)	Convection and radiation to the surrounding air Conduction to the internal elements (only from the part "seen" by the fire)	
Eventual wall layers (solid)	Conduction	Conduction	
Internal layers of storage tank (including cover and bottom)	Conduction through the tank wall	Convection to liquid or vapour Radiation to vapour from internal surface of elements "seen" by fire	
Liquid	Convection and conduction from internal surface of elements "seen" by fire Convection with vapour	Convection and conduction to internal surface of elements not "seen" by fire Convection to the bottom of the tank, evaporation/boiling to vapour	
Vapour	Convection, conduction and radiation from internal surface of elements of tank wall + cover "seen" by fire Evaporation/boiling from liquid	Convection and conduction to internal surface of elements of tank wall + cover not "seen" by fire Convection with liquid	
Bottom of the tank when in contact with the ground	Convection from liquid	Conduction to the base which is assumed to maintain ambient temperature	

Table 1

#### Heat transmission mechanisms in the different parts of the system

# 2.3. Effect of heat input to the stored product

The result of the heat input to the storage tank is to continuously increase the temperature of the tank content both in liquid and vapour spaces. Evaporation takes place as long as the liquid temperature is lower than the boiling point of the substance. After a certain period of time the liquid temperature reaches the boiling point at the corresponding pressure conditions. The evaporated mass produced causes an increase of pressure in the vapour space. Boiling is inhibited and liquid heating associated with evaporation is taking place until boiling starts again. So, there is continuously a transition from the evaporating regime to the boiling regime and back again to the evaporation and so on until the vapour pressure reaches the set pressure of the safety valve.

At this point the safety valve starts opening relieving a certain amount of gas from the vapour space. This transition regime prevails until an equilibrium is reached at the



Fig. 1. Tank division in elements.

point that the vapour relieved through the safety valve has taken away the total net heat input to the tank. At such conditions temperature and pressure in the tank remain constant. The maximum pressure achieved this way cannot exceed the safety valve set pressure plus allowable accumulation (corresponding to a fully open safety valve). If however the safety valve cannot release to the environment the necessary amount of vapour then the temperature and pressure of the tank content will keep on increasing until the tank fails. Finally, it must be noted that heat can also be taken out from the tank by pumping out liquid product.

In the following a detailed description of the model is given including assumptions and equations used.

#### 3. Mathematical modelling

For the mathematical modelling the tank wall is divided in elements as shown in the Fig. 1. For simplifying the calculations only half of the tank is considered taking into account its symmetry. Each element is characterised by the (i, j, k) indices. The radial distribution of the tank components is indicated by the index j (see Fig. 1). Each layer can be subdivided into various arc elements corresponding to the various values of index i. Index k is used to notify whether the part of the wall is in contact with the liquid or the vapour phase of the substance. k takes two values:  $k = \ell$  for the liquid and k = v for the vapour space. The number of elements in both directions can be increased and then a finite element analysis should be used to get a rigorous description of the temperature profiles over time in the tank.

A good approximation at reduced computational time can be achieved by splitting the tank in various sectors. Physical layers (e.g. layers of tank wall, content of tank) are considered in the radial direction. The angular distribution is based on sectors receiving a certain uniform heat input within angle  $\theta$ .

Each element is assumed to have uniform temperature and the equation of the next paragraph can be applied. The same approach is adopted for the cover and the bottom of the tank; the only difference being that the cover is always in contact with the vapour phase of the substance and the bottom with the liquid, so only indices (i, j) are used.

Modelling of the heat transfer phenomena referred to in Sections 2.1 through 2.3 is described here.

#### 3.1. Heat transfer

The wall of the tank is divided in elements as already described. Each element is characterised by three indices i, j, k.

For the calculation of the temperatures of all the system parts the equation used is:

$$\frac{dT_{(i, j, k)}}{dt} = \frac{1}{c_j m_{(i, j, k)}} (Q_{\rm in} - Q_{\rm out}), \tag{4}$$

where

- $T_{(i, j, k)}$  is the temperature of (i, j, k)th element,
- $c_j$  is its heat capacity,  $m_{(i, j, k)}$  its mass and
- $Q_{in} Q_{out}$  is the rate of energy in and out of that element.

What the former equation expresses is that the temperature increase rate of every wall element depends on the net rate of energy in and out of that element.

In this way a set of differential equations is produced containing equations describing the temperature dependence of each element. This set of differential equations is then solved by using the GEAR ordinary differential equations solver [16].

The analytical expressions of the finite difference forms for each element of the system are derived from Eq. (4) where the appropriate expressions for  $Q_{in}$  and  $Q_{out}$  are used according to the dominating mechanisms of heat transfer already described in Table 1. More precisely we have for the temperature of the element (i, j, k):

$$\frac{\mathrm{d}T_{(i, j, k)}}{\mathrm{d}t} = \frac{1}{c_{j}m_{(i, j, k)}} \left( Q_{\mathrm{F}_{i}}A_{\mathrm{surf}} + a_{1}\frac{k_{j}}{x_{i, j}}(T_{i, j-1, k} - T_{i, j, k})A_{\mathrm{surf}} + a_{2}\frac{k_{j}}{u_{i, j}}(T_{i-1, j, k} - T_{i, j, k})A_{i} + a_{3}\frac{k_{j}}{h}(T_{i, j, v} - T_{i, j, k})A_{k} - a_{4}\frac{k_{j}}{x_{i, j}}(T_{i, j, k} - T_{i, j-1, k})A_{\mathrm{surf}} - a_{5}\frac{k_{j}}{u_{i, j}}(T_{i, j, k} - T_{i-1, j, k})A_{i} - a_{6}n_{s}E_{\mathrm{out}}\sigma(T_{i, n_{w}, k}^{4} - T_{\mathrm{amb}}^{4})A_{\mathrm{surf}} - a_{7}n_{s}E\sigma(T_{i, 1, k}^{4} - T_{k}^{4})A_{\mathrm{surf}} - a_{8ns}H_{\mathrm{wk}}(T_{i, i, k} - T_{k})A_{\mathrm{surf}} - a_{9}n_{s}\frac{k_{k}}{R}(T_{i, j, k} - T_{k})A_{\mathrm{surf}} - a_{10}n_{s}H_{\mathrm{w}}(T_{i, n_{w}, k} - T_{\mathrm{amb}})A_{\mathrm{surf}} \right).$$
(5)

In (5)  $T_{i, j, k}$  is the temperature of the (i, j, k)th element;  $k_j$  is the thermal conductivity for every element;  $k_k$  is the thermal conductivity of the liquid when  $k = \ell$  or that of the vapour when k = v;  $x_{ij}, u_{ij}, h$  are the distances between different elements and  $A_{surf}$ ,  $A_i, A_k$  are the surfaces between the different elements, R is the radius of the tank.  $E_{out}$  is the outer wall emissivity; E is the internal wall emissivity;  $\sigma$  is the Stefan-Boltzmann constant;  $T_{amb}$  is the ambient temperature;  $n_s$  is the maximum value of the *i* index;  $n_w$  is the maximum value of the *j* index; and  $k = \ell$  or v when referring to the elements in contact with liquid/vapour respectively.

 $H_{wk}$  is the heat transfer coefficient by convection and takes the value of  $H_{w\ell}$  for  $k = \ell$  or  $H_{wv}$  when k = v;  $H_w$  is the heat transfer coefficient between the external wall layer and the ambient air. The expressions that give the values of all temperature dependent heat transfer coefficients including the case of nucleate boiling, are similar to those used in other models (i.e. ENGULF), and they are described in Ref. [17].

The  $a_1, \ldots, a_{10}$  are constants assuming the values of 0 or 1 when necessary, according to the boundary conditions for every element.

Similar to (5) equations are used for the cover and the bottom of the tank. In this case, since the number of layers constituting the cover and the bottom of the tank can be different from  $n_w$ ,  $n_c$  and  $n_b$  are used respectively.

Together with the equations generated by (5) the equations for the temperature of the liquid and the vapour consist the set of the differential equations. It is assumed that there is no temperature gradient in both phases of the substance stored. Temperatures  $T_{\ell}$  (for the liquid) and  $T_{\nu}$  (for the vapour) are only time dependent. The time dependent  $T_{\ell}$ ,  $T_{\nu}$  are assumed to be uniformly distributed in both the liquid and the vapour phase of the substance.

Due to the evaporation and/or boiling, heat  $(Q_B)$  is added to the vapour from the liquid.  $Q_B$  is given by:

$$Q_{\rm B} = \lambda m_{\rm E}.\tag{6}$$

The rate of energy loss from the vapour space due to the operation of the safety valve  $Q_s$ , is given by:

$$Q_{\rm S} = c_{\rm v} m_{\rm S} T_{\rm v}. \tag{7}$$

The rate of energy loss from the liquid space due to the mass pumped out of the tank  $Q_{\rm P}$ , is given by:

$$Q_{\rm P} = c_\ell m_{\rm P} T_\ell, \tag{8}$$

where  $c_{\ell}, c_v, m_{\ell}, m_v$  are the heat capacities and the masses of the liquid and the vapour respectively;  $\lambda$  is the latent heat of evaporation for the substance stored;  $m_E$  is the rate of mass transferred from the liquid to the vapour by evaporation/boiling;  $m_P$  is the rate of mass pumped out;  $m_S$  is the rate of vapour mass relieved through the safety valve.

So, the time dependent temperature variations of the liquid and the vapour, taking into account the heat transfer mechanisms described in Table 1 and those described above, are given by:

$$\frac{dT_{\ell}}{dt} = \frac{1}{c_{\ell}m_{\ell}} \left( n_{\rm s}H_{\rm wk}(T_{i,1,\ell} - T_{\ell})A_{\rm surf} + n_{\rm s}\frac{k_{\ell}}{R}(T_{i,1,\ell} - T_{\ell})A_{\rm surf} + n_{\rm s}E\sigma(T_{i,1,\ell}^4 - T_{\ell}^4)A_{\rm surf} + H_{\ell\nu}(T_{\rm v} - T_{\ell})A_{\rm b} - \lambda m_{\rm E} - c_{\ell}m_{\rm P}T_{\ell} \right). \quad (9)$$

$$\frac{dT_{\rm v}}{dt} = \frac{1}{c_{\rm v}m_{\rm v}} \left( n_{\rm s}H_{\rm wv}(T_{i,1,\rm v} - T_{\rm v})A_{\rm surf} + n_{\rm s}\frac{k_{\rm v}}{R}(T_{i,1,\rm v} - T_{\rm v})A_{\rm surf} + n_{\rm s}E\sigma(T_{i,1,\rm v}^4 - T_{\rm v}^4)A_{\rm surf} - H_{\ell\nu}(T_{\rm v} - T_{\ell})A_{\rm b} + \lambda m_{\rm E} - c_{\rm v}m_{\rm S}T_{\rm v} \right). \quad (10)$$

In Eqs. (9) and (10)  $H_{\ell v}$  is the heat transfer coefficient between liquid and vapour;  $A_b$  the interaction surface between liquid and vapour.

### 3.2. Mass balance

For the evaluation of the mass balance within the tank the vapour is assumed to behave as a perfect gas. Once equilibrium between the liquid and the vapour is lost, because of the increase in temperature, evaporation occurs from the surface of the liquid. The driving force is the difference between the vapour pressure  $P_v$  and the partial pressure of the substance vapours in the vapour space  $P_G$ ,  $(P_v - P_G)$ . So,  $m_E$  is given by the equation [17, 18]:

$$m_{\rm E} = K_{\rm G} M_{\rm B} (P_{\rm v} - P_{\rm G}), \tag{11}$$

where  $K_G$  is the mass diffusion coefficient which may be calculated from its relation with the heat transfer coefficient corresponding to convection between the liquid and the vapour and  $M_B$  is the molecular weight of the substance.

The vapour pressure  $P_v$  is determined by the physical properties of the substance and the temperature. For most pure substances it may be calculated with adequate accuracy by using the Antoine equation [19].

The partial vapour pressure in the vapour space  $P_G$  depends on the total pressure and on the molar fraction at the ullage space of the storage tank. For the calculation of  $P_G$  the following assumptions are made: (1) Gases in the ullage space behave as perfect gases; (2) Dalton's law applies for the gas mixture in the ullage space of the tank.

Evaporation of the liquid mass occurs until the temperature of the liquid becomes equal to its boiling point corresponding to the vapour pressure in the ullage space of the tank. During boiling the temperature of the liquid remains constant and therefore the rate of liquid evaporated can be obtained from Eq. (9) solved for  $m_{\rm E}$  where  $dT_{\ell}/dt$ equals zero.

However as the mass of vapour in the ullage space increases the overall pressure increases too. This results in an increase in the boiling point. Consequently boiling is inhibited until the liquid temperature rises to the new boiling point. Therefore a continuous transition from boiling to evaporation and vice versa occurs until a constant pressure is established in the tank. Consequently an average evaporation rate can be obtained by solving simultaneously the heat balance equations for liquid and vapour.

Due to mass transfer from liquid to vapour and eventual mass transport from the tank through either the safety valve or the pump out system the masses of the liquid and vapour change continuously. Masses are considered constant within a time step and are adjusted at the end of each time step  $\Delta t$  according to the following equations:

$$m_{\ell} = m_{\ell 0} - m_{\rm E} \Delta t - m_{\rm P} \Delta t, \tag{12}$$

$$m_{\rm v} = m_{\rm v0} + m_{\rm E}\Delta t - m_{\rm S}\Delta t. \tag{13}$$

The following parameters  $c_\ell$ ,  $c_v$ ,  $c_j$ ,  $H_{v\ell}$ ,  $H_{wk}$ ,  $H_w$ ,  $k_j$ ,  $K_G$ ,  $\lambda$ ,  $\rho_j$ ,  $\rho_\ell$ ,  $\rho_v$  are temperature dependent. There are various empirical formulas describing the temperature dependence of these parameters in the literature [19-21]. However different formulas are applicable for different substances and generally no universal applicable formulas can be established.

# 3.3. Generation of system's equations

The number of equations, N, to be integrated is given by:

$$N=2n_{\rm s}n_{\rm w}+n_{\rm s}n_{\rm c}+n_{\rm s}n_{\rm b}+2,$$

where  $n_s$  is the maximum number of sectors in which the symmetrical tank is divided. It is equal to  $\pi/\theta$  where  $\theta$  is the angle of the generic sectors;  $n_w$  is the maximum number of layers making up the lateral wall of the tank.

Therefore,  $2n_s n_w$  is the number of equations governing the heat balance on the lateral surface of the tank.  $n_c$ : is the maximum number of layers making up the cover of the tank, which can be different from  $n_w$ . Thus  $n_s n_c$  is the number of equations governing the heat balance of the cover.  $n_b$ : as  $n_c$ , but for the bottom of the tank. So,  $n_s n_b$  is the number of equations governing the heat balance of the cover.  $n_b$ : as  $n_c$ , but for the bottom of the tank. So,  $n_s n_b$  is the number of equations governing the heat balance of the tank. So,  $n_s n_b$  is the number of equations describing the physical phenomena in liquid and vapour phase of the substance stored.

It can be seen that in practical situations it may be too cumbersome for the user to write down the set of equations. For example, for a tank with three lateral layers, two cover layers and two bottom layers, with  $n_s$  equal to four (which is the minimum to have acceptable results), the number of equations is 42.

For this reason, an algorithm for the automatic generation of the set of differential equations has been developed. This algorithm generates the set of differential equations in matrix form:

$$|\dot{Y}(i)| = |P(i,j)| \cdot |Y(j)| + |Q(i,j)| \cdot |Y^{4}(j)| + |K(i)|,$$
(14)

where i, j = 1, 2, ..., N; Y is the array of temperatures; P and Q are the arrays of coefficients and K is the array of constants.

Therefore the *i*th equation is given by:

$$\dot{Y}(i) = \sum_{j=1}^{N} P(i,j) \cdot Y(j) + \sum_{j=1}^{N} Q(i,j) \cdot Y^{4}(j) + K(i).$$
(15)

For the construction of the system of equations the algorithm needs simple data such as: initial temperatures; thermal properties of the different layers of the storage tank; tank geometry.

#### 4. Software development

Based on the above described mathematical formulation of the model a computer program has been developed in FORTRAN 77 programming language. The program runs in a personal computer 486, 50 MHz and for comparison purposes it is referred that a simulation for a time period of 5000 s and for the below described example the total execution time is approximately one hour. This time corresponds to 5000 calls of the integrator routine for the set of the sixty-two differential equations of the following example. The simplified flow diagram of the code is shown in Fig. 2.

#### 5. Example of model application

Based on the above, an application of the model has been performed. A fire in a tank farm threatening an ammonia cryogenic storage tank has been considered. The heat is generated by a tank/pool fire in the vicinity of the tank. Distances between storage tanks according to the NFPA 30-1984 regulations [22] have been considered. This tank was also used as part of the reference plant for the Benchmark Exercise on Major Hazard Analysis organised by CEC/JRC-Ispra/ISEI [23].

The storage tank which consists of a single steel plate wall is cylindrical with a curved roof. It is 31 m high and has an inside diameter of 33.8 m. The steel tank is insulated with 100 mm of polyurethane on the shell and the roof and 150 mm of foam glass on the bottom. The tank is located within an outer concrete tank. The concrete tank has a wall thickness of 250 mm and is supported about 1 m above ground on 112 support legs each 1 m diameter. It protects the main tank and serves as a retention tank in case of a tank rupture. The tank is designed for storing 15000 t of ammonia at about 239 K ( $\sim -33$  °C).

The tank is equipped with a pressure valve according to the API 2000 standard for venting atmospheric and low pressure storage tanks (gauged at 150 g eff.).

The tank receives heat input from an adjacent tank fire. It is assumed that the fire temperature is 1500 K. As previously explained all calculations are performed taking into account only half of the tank and for the rest symmetry is assumed. The part of the tank examined is divided in four sectors. It is assumed that only the two sectors facing the fire are receiving heat input, the third sector is receiving a very small amount, and the fourth sector is not receiving heat input from radiation.



Fig. 2. Flow diagram of the program. Here t represents time,  $t_{max}$  the maximum time for calculations and  $t_{out}$  the time instants for results output.

So, in this case  $n_w = 4$ ,  $n_c = 4$ ,  $n_b = 3$  and  $n_s = 4$ . The first layer of the lateral wall as well as that of the bottom and the cover is steel. The second layer of the lateral wall and the cover is polyurethane and that of the bottom is foam glass. The third layer is air for the lateral wall and the cover and concrete for the bottom. The fourth layer is made of concrete for the lateral wall and from steel for the roof. The thermal properties of each of the layers are given in the input file.

In the following the time dependence of the physical properties of the substance stored are given.



Fig. 3. Time dependence of temperature of the  $n_c = 1$ ,  $n_s = 1$  element.

#### 5.1. Discussion of the results

In Fig. 3 the time dependence of the temperature of the first layer of the cover is shown. The initial temperature of that element  $(n_c = 1, n_s = 1)$  is equal to the storing temperature of ammonia, thus 239 K. We can see the effect of the insulating layers (air-polyurethane), since the temperature of the element rises slowly compared to the heat input that the last layer  $(n_c = 4, n_s = 1)$  receives.

In Fig. 4 the time dependence of the temperature of the ammonia vapour is shown. The effect of the opening of the safety valve is clearly shown. As a matter of fact when the safety valve opens, which for the first time happens at  $\sim 47$  min, the temperature of the vapour falls and then it increases again until the safety valve opens again. In this way the mass of the vapour decreases and its overall temperature increases (independently of the operation of the safety valve).

In Fig. 5 the liquid ammonia temperature as a function of time is presented. It can be noticed that the liquid temperature is increasing very slowly compared to that of the vapour. This is due to the large mass of liquid ammonia and its larger heat capacity from the ammonia vapour.

In Fig. 6 the total pressure in the vapour space of the tank is shown as a function of time. The effect of the safety valve is clearly shown. When the value of the pressure exceeds the value of the set pressure for the safety valve, the safety valve opens relieving a certain amount of ammonia vapour. This results in a sudden fall of the internal tank pressure. However, when the temperature of the liquid reaches to the point where boiling starts for the pressure above the liquid ( $\sim 77 \text{ min}$ ), the mass of the



Fig. 4. Time dependence of temperature of ammonia vapour.



Fig. 5. Time dependence of temperature of liquid ammonia.



Fig. 6. Time dependence of total pressure in vapour space.

vapour increases rapidly and the operation of the safety value is not enough to maintain the pressure between the desired limits. At this point we have failure of the storage tank due to overpressure.

In Fig. 7 the accumulative mass of ammonia released from the safety value is shown. When boiling of the liquid starts the safety value remains open in order to release as much vapour as possible.

### 6. Conclusions

In this paper a model which describes the time dependence of the physical properties of a cryogenic storage tank receiving heat from an adjacent burning tank is described. Various influencing parameters (tank size, tank spacing, filling height, existence of mitigation measures i.e. cooling ring, water curtains, and operational interventions such as liquid product pump out etc.) have been included in the model formulation. The model can be used to:

- evaluate the effectiveness of different mitigating features;
- predict the time that a failure might occur;
- evaluate the impact of various contingencies;
- evaluate the effectiveness of various protective action strategies.

The model can be easily adjusted to consider other heat input mechanisms as well as other types of storage tanks.



Fig. 7. Total amount of ammonia released.

The model is implemented on a personal computer (DOS operating system) and has been written in Fortran 77 (Microsoft 5.1).

Among our future plans validation of the model is foreseen, provided that experimental data are available. For the time being there is a lack of experimental data since full scale experiments for the consequences of fire to storage tanks are now being done. Also, in order to improve the software developed, future work will concentrate upon the development of a user friendly interface with graphic capabilities for the 2D/3D description of the plant layout on which the results should be graphically displayed.

Finally, it is planned that the model developed will be incorporated in the DOM-INO package [24] which is able to simulate accident evolution sequences in chemical installations and identify subsequent events leading to escalation.

# 7. Nomenclature

$a_1, \ldots, a_{10}$	constants used for determining the boundary conditions of each element
$A_1$	surface of the target $(m^2)$
$A_2$	surface of the fire $(m^2)$
Aь	surface between liquid-vapour, bottom surface (m <sup>2</sup> )
$A_i$	surface between $i, i + 1$ elements (m <sup>2</sup> )
A <sub>surf</sub>	surface between the different $j, j + 1$ elements (m <sup>2</sup> )
A.	surface between <i>i</i> , <i>i</i> , $\ell/i$ , <i>i</i> , <i>y</i> elements (m <sup>2</sup> )

c <sub>i</sub>	heat capacity of the <i>j</i> th element $(J/(kg K))$
$C_{\ell}, C_{v}$	the heat capacities of the liquid and the vapour respectively (J/kg K)
Ε	internal wall emissivity
$E_{\rm out}$	outer wall emissivity
F	view factor
h	distance between $i, j, \ell/i, j, v$ elements (m)
H <sub>lv</sub>	heat transfer coefficient by convection between vapour and liquid
	$(W/(m^2 K))$
H <sub>w</sub>	heat transfer coefficient between wall outer surface and air $(W/(m^2 K))$
$H_{w\ell}$	heat transfer coefficient by convection between wall and liquid
	$(W/(m^2 K))$
k;	thermal conductivity of the <i>i</i> th element (W/(m K))
κ <sub>G</sub>	mass diffusion coefficient (mol/(h atm ft <sup>2</sup> )
m <sub>F</sub>	rate of mass transferred from the liquid to the vapour by
2	evaporation/boiling (kg/s)
m;;r	mass for the $(i, j, k)$ th element (kg)
$m_{2}, m_{3}$	masses of the liquid and the vapour respectively (kg)
$m_{\ell 0}$	mass of the liquid at previous time step (kg)
m <sub>P</sub>	rate of mass pumped out (kg/s)
ms	rate of vapour mass relieved through the safety valve (kg/s)
$m_{v0}$	mass of the vapour at previous time step (kg)
$\dot{M_{\rm B}}$	molecular weight of the substance (g/mol)
$n_{\rm c}$	number of cover layers
$n_{\rm b}$	number of bottom layers
$n_{s}$	maximum value of the <i>i</i> index
ก้	number of lateral layers of the storage tank
P <sub>G</sub>	partial pressure of the substance vapours at the vapour space (Pa)
$P_{\rm v}$	pressure of the vapour at the vapour-liquid interface (Pa)
$Q_{\rm B}$	rate of energy transferred from the liquid space to the vapour due to the
	evaporation/boiling mechanism (J/s)
$Q_{\rm E}$	rate of heat transmitted from the fire by radiation $(J/(m^2 s))$
$Q_{\rm F}$	rate of heat arriving on the target surface by radiation $(J/(m^2 s))$
$\overline{Q}_{in}$	rate of heat input in the system parts by all heat transfer mechanisms (J/s)
Qout	rate of heat output of the system parts by all heat transfer mechanisms
	(J/s)
$Q_{P}$	rate of energy deducted from the liquid space due to the mass pump out
	operation (J/s)
$Q_{\rm S}$	rate of energy deducted from the vapour space due to the operation of the
	safety valve (J/s)
u <sub>ij</sub>	distance between the elements $i, i + 1$ (m)
Tamb	ambient temperature (K)
T <sub>f</sub>	flame temperature (K)
$T_{(i, j, k)}$	temperature of the $(i, j, k)$ th element (K)
$T_{\ell}$	temperature of the liquid (K)
T	to $\mathbf{v}$ and $\mathbf{v}$ of the version $(\mathbf{V})$

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 $T_{\rm v}$  temperature of the vapour (K)

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Y	array of temperatures (K)
x <sub>ij</sub>	distance between the elements $j, j + 1$ (m)

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absorptivity of the target
flame emissivity
angles made by the outward normals to the planes $dA_1$ , $dA_2$ with the line joining the two elemental areas
angle used for the division of the tank in <i>i</i> elements
latent heat of evaporation for the substance stored (J/kg)
density of the <i>i</i> th element $(kg/m^3)$
densities of liquid, vapour respectively (kg/m <sup>3</sup> )
Stefan-Boltzmann constant (J/(m <sup>2</sup> K <sup>4</sup> s))
air transmissivity

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