

## MODELING RUNAWAY REACTIONS IN REACTORS PROTECTED WITH SUPPRESSION SYSTEMS

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### Summary

A mathematical model has been developed for simulating the operation of a system for the protection of chemical reactors against runaway reactions, which is based on containment and *in situ* quenching with an inert diluent.

The model has been evaluated with physical and chemical data taken from the literature. The early detection of the runaway and the allowance for a suitable gaseous freeboard are the two main factors to be considered.

In the case examined, which may be considered representative of a large number of real cases, the protection of the reactor appeared possible with reasonable values of the two above mentioned factors.

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### List of symbols

- A, B* constants in the vapour pressure equation  
*C* heat capacity,  $\text{kJ kg}^{-1} \text{K}^{-1}$   
*D* density,  $\text{kg m}^{-3}$   
*E* energy,  $\text{kJ mol}^{-1}$   
*F* degree of filling  
*H* enthalpy,  $\text{kJ kg}^{-1}$   
*k* pre-exponential factor,  $\text{s}^{-1}$   
*M* mass, kg  
*P* pressure, MPa  
*R* gas constant,  $\text{kJ mol}^{-1} \text{K}^{-1}$   
*T* temperature, K  
*V* volume,  $\text{m}^3$   
*X* degree of conversion  
*Y* weight fraction of solvent in the gaseous phase

### Greek symbols

- $\vartheta$  dimensionless temperature

$\mu$	dimensionless mass
$\nu$	reaction order
$\pi$	dimensionless pressure
$\rho$	dimensionless density
$\tau$	dimensionless time
$\chi$	dimensionless group
$\psi$	functions

### *Subscripts*

A	actuated	L	liquid phase
AC	activation	O	initial
C	characteristic	R	reactant, reaction
E	explosion	S	suppressor
F	final	V	vapour, vaporization
G	gaseous phase		

## **Introduction**

The safe operation of chemical plants requires, *inter alia*, effective measures for the protection of chemical reactors against the effects of explosions generated by runaway reactions. In the past decade a great deal of work has been carried out on this subject [1,2].

The different aspects of the runaway were considered and recommendations were proposed to take into account the boiling of the liquid phase, the venting of two-phase flashing mixtures and the disposal of the effluents. At present, this work cannot be easily turned into simple design procedures, because of the lack of detailed knowledge on the physical and chemical phenomena involved, which are often very complex and not easily arranged into a general framework. However, the relevant results are very useful to attempt the simulation of the runaway by means of mathematical models, which should be used to support the experimental work and the design procedures [3-8].

Most information is available on the problems relating to the sizing of the bursting disc. Irrespective of its importance, the disposal of the effluents attracted the attention of the researchers to a smaller extent. Nevertheless, if the quenching effect of the depressurization is unable to nullify the chemical reactivity, a pressure and shock resistant blow-down system must be provided. Moreover, the catchtank must be suitably sized to hold the vessel contents and the required amount of suppressor. This is particularly the case of toxic and/or flammable effluents which of course cannot be directly discharged into the sewer [9].

These requirements result in a cost for the blow-down system which can represent a not inconsiderable fraction of the total cost of the reactor. Therefore, an alternative method of protection, based on the containment of the

explosion and on the inerting *in situ* of the reactive mixture through the injection of a suitable amount of inert diluent, should be considered at least when very dangerous chemicals are handled.

In the study presented in this paper a lumped-parameter mathematical model was developed and run, using a realistic set of physical and chemical data [10], to assess the effectiveness of the proposed protection system.

### Mathematical model

The model is written with reference to a batch reactor, partially filled with a liquid phase, in which a non-gassy runaway reaction occurs. The gaseous phase mainly consists of vapours of the liquid solvent, whereas the allowance for a small amount of inerts makes the initial pressure independent of the initial temperature. The conservative hypothesis of adiabaticity is assumed. Therefore, no true steady-state is possible and any state of the system is considered stable if the relevant explosion delay (lag-time) assumes a suitably high value.

The time evolution of the runaway is described by a system of three ordinary differential equations (ODEs), written for the three main variables, namely the degree of conversion, the temperature and the vaporized mass. Two different periods can be singled out. The first period lasts from the starting time to the time at which the suppression system is actuated. This system is active until the temperature attains a *safe* value  $T_F < T_0$  (to be defined later) or alternatively, until the reactor is almost entirely filled with the liquid phase. In the first instance, the inerting was successful.

In addition to the main variables, the following secondary variables are introduced:

a) the mass of the gaseous phase, given by

$$M_G = M_{G0} + M_V \quad (1)$$

b) the mass of suppressor discharged into the reactor, which is obviously set equal to zero during the first period. During the second period it is assumed that

$$M_S = (dM_S/dt) \times (t - t_A) \quad (2)$$

where the suppressor flow rate is treated as a constant input variable. For  $t > t_F$ , the mass of suppressor is kept constant at the value

$$M_{SF} = (dM_S/dt) \times (t_F - t_A) \quad (3)$$

c) the mass of liquid solution. From a simple mass balance one obtains

$$M_L = M_{L0} - M_V + M_S \quad (4)$$

d) Introducing the liquid-phase density,  $D_L$ , the volume taken up by the liquid phase yields

$$V_L = M_L / D_L \quad (5)$$

e) the total pressure, given by

$$P = P_0 \times (M_G / M_{G0}) \times (T / T_0) \times (V_{G0} / (V - V_L)) \quad (6)$$

f) the vapour pressure of the solution. Since only the constant-volatility case is considered, a simple exponential relationship holds

$$P_L = \exp(A - B/T) \quad (7)$$

in which  $A$  and  $B$  are independent of the liquid-phase composition.

g) the solvent mass fraction in the gaseous phase is given by

$$Y = (M_V + Y_0 M_{G0}) / M_G \quad (8)$$

The system of ODEs consists of the following three equations:

a) *kinetic equation*

A simple runaway reaction of Arrhenius-type kinetics and order  $\nu$  in the mass fraction of the reactant is assumed. With the usual definition of degree of conversion

$$X = (M_{R0} - M_R) / M_{R0} \quad (9)$$

it results

$$dX/dt = k \times \exp(-E_{AC}/RT) \times (M_{R0}/M_L)^{\nu-1} \times (1-X)^\nu \quad (10)$$

b) *energy balance equation*

In the hypothesis of adiabaticity, the energy balance reads

$$M_{R0}(-\Delta H_R)(dX/dt) = (M_L C_L + M_G C_G)(dT/dt) + \Delta H_V(dM_V/dt) + C_S(T - T_S)(dM_S/dt) \quad (11)$$

where  $T_S$  is the inlet temperature of the suppressor. Obviously, the last term at the righthand side is set equal to zero when the suppression system is inactive.

c) *equilibrium equation*

The usual Raoult equation

$$YP = P_L \quad (12)$$

is used to model the liquid–vapour equilibrium for the solvent. This equation holds in the hypothesis that the mass fraction of the solvent in the vapour phase is essentially equal to its mole fraction. This simplifying hypothesis avoids the introduction of two more parameters (i.e. the molecular weights of both solvent and inerts), whose effect is certainly very small.

Equation (12) is used in the model in its differential form

$$Y(dP/dt) + P(dY/dt) = dP_L/dt \quad (13)$$

where the secondary variables  $P$ ,  $P_L$  and  $Y$  and their derivatives are written as explicit functions of the main variables through the relevant equations of definition.

The initial conditions for the main variables are obviously

$$\text{at } t=0, \quad X=0, \quad M_V=0, \quad T=T_0 \quad (14)$$

whereas the initial values of the secondary variables are conveniently fixed in connection with the definition of the dimensionless variables

$$\vartheta = T/T_0, \quad \mu = M/M_C, \quad \pi = P/P_0, \quad \rho = D/D_C, \quad \tau = t/t_C \quad (15)$$

A suitable definition of the characteristic mass is given in terms of the characteristic density, which is assumed equal to the initial value of the gaseous-phase density. Therefore

$$M_C = D_C V \quad (16)$$

The initial values of the dimensionless masses in the reactor can now be defined in terms of the initial degree of filling

$$F = V_{L0}/V \quad (17)$$

as

$$\mu_{G0} = 1 - F \quad (18)$$

$$\mu_{L0} = \rho_L F \quad (19)$$

The definition of the characteristic time follows from the dimensionless kinetic equation, which can be written as

$$\dot{X} = dX/d\tau = \exp(\chi_{AC}(\vartheta - 1)/\vartheta) \mu_L^{1-\nu} (1 - X)^\nu = \psi_1 \quad (20)$$

where

$$\chi_R = M_{R0}/M_{L0} \quad (21)$$

$$\chi_{AC} = E_{AC}/RT_0 \quad (22)$$

and

$$t_C = (\chi_R \rho_L F)^{1-\nu} / (k \exp(\chi_{AC})) \quad (23)$$

With a similar procedure, the dimensionless equation of energy balance is written as

$$\psi_2 \dot{\vartheta} + \psi_3 \dot{\mu}_V + \psi_4 - \dot{X} = 0 \quad (24)$$

where  $\vartheta = d\vartheta/d\tau$ ,  $\dot{\mu}_V = d\mu_V/d\tau$  and

$$\psi_2 = T_0(C_L\mu_L + C_G\mu_G)/\text{DEN} \quad (25)$$

$$\psi_3 = \Delta H_V/\text{DEN} \quad (26)$$

$$\psi_4 = T_0 C_S (\vartheta - \vartheta_S) \dot{\mu}_S / \text{DEN} \quad (27)$$

with

$$\text{DEN} = \chi_R \rho_L F(-\Delta H_R) \quad (28)$$

Finally, the dimensionless equation of equilibrium is derived from eqn. (13) in the form

$$\psi_5 \dot{\vartheta} + \psi_6 \dot{\mu}_V + \psi_7 = 0 \quad (29)$$

with

$$\psi_5 = (Y\rho_L\mu_G)/\text{DEN} - \pi_S\chi_{V2}/\vartheta^2 \quad (30)$$

$$\psi_6 = \pi(1-F)(1-\pi_{L0})/(\mu_V + 1-F)^2 + Y\rho_L\vartheta(1-\mu_G/\text{DEN})/\text{DEN} \quad (31)$$

$$\psi_7 = Y\rho_L\dot{\mu}_S\vartheta\mu_V/\text{DEN}^2 \quad (32)$$

and

$$\text{DEN} = \rho_L - \mu_L \quad (33)$$

In these equations, the following dimensionless variables are used

$$\pi = (\rho_L\mu_G\vartheta)/(\rho_L - \mu_L) \quad (34)$$

$$\pi_L = \exp(\chi_{V1} - \chi_{V2}/\vartheta) \quad (35)$$

with

$$\chi_{V1} = A - \ln(P_0) \quad (36)$$

$$\chi_{V2} = B/T_0 \quad (37)$$

and

$$Y = (\mu_V + Y_0\mu_{G0})/\mu_G \quad (38)$$

with

$$Y_0 = \pi_{L0} = P_{L0}/P_0 \quad (39)$$

An explicit form of the system (20) (24) (29) can be easily derived and integrated using a fourth-order Runge-Kutta method and the initial conditions

$$\text{at } \tau=0, X=0, \vartheta=1, \mu_V=0 \quad (40)$$

## Results and discussion

The model described in the previous Section was developed in order to obtain the most simple, non trivial picture of the runaway in a batch reactor. Even if many details (e.g. fluid dynamic phenomena) were omitted, the number of parameters to be considered is so high that an exhaustive analysis of sensitivity would be very complex and essentially meaningless. Therefore, the model was run using the physical and chemical properties of the phenol-formaldehyde system, used in the manufacture of phenolic resins and studied by Booth et al. [10]. The input data used are reported in Table 1.

A first set of results, shown in Figs. 1 to 3, refers to the runaway in absence of any protection system. The dimensionless temperature is plotted against the dimensionless time in Fig. 1, for different values of the initial temperature.

TABLE 1

Input data used

$C_L$	=	2.90 kJ kg <sup>-1</sup> K <sup>-1</sup>
$C_G$	=	1.88 kJ kg <sup>-1</sup> K <sup>-1</sup>
$\Delta H_V$	=	2503 kJ kg <sup>-1</sup>
$D_L$	=	1024 - 0.673 $T$ (°C) kg m <sup>-3</sup>
$-\Delta H_R$	=	2.7 GJ kg <sup>-1</sup>
$k$	=	7.95 10 <sup>8</sup> s <sup>-1</sup>
$E_{AC}$	=	103 kJ mol <sup>-1</sup>
$\nu$	=	2
$P_0$	=	0.1013 MPa
$F_0$	=	0.824
$\chi_{R}''$	=	0.156
$A$	=	11.47
$B$	=	5133 K <sup>-1</sup>
$\dot{\mu}_S$	=	50,000
$C_S$	=	4.18 kJ kg <sup>-1</sup> K <sup>-1</sup>

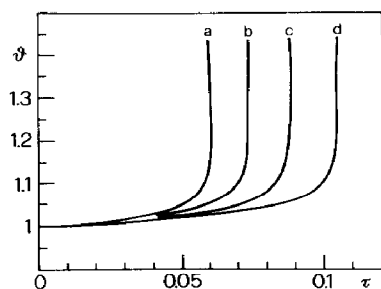


Fig. 1. Dimensionless temperature  $\vartheta = T/T_0$  against the dimensionless time  $\tau = t/t_C$  for different values of the initial temperature  $T_0$ . (a)  $T_0 = 30^\circ\text{C}$ ; (b)  $T_0 = 50^\circ\text{C}$ ; (c)  $T_0 = 70^\circ\text{C}$ ; (d)  $T_0 = 90^\circ\text{C}$ .

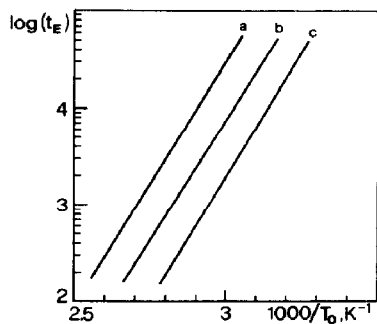


Fig. 2. Explosion delay  $t_E$  (s) against the inverse of the initial temperature  $T_0$  (K), for three different values of the concentration ratio  $\chi_R = M_{R0}/M_L$ . (a)  $\chi_R = \chi_R^0/2$ ; (b)  $\chi_R = \chi_R^0$ ; (c)  $\chi = 2\chi_R^0$ .

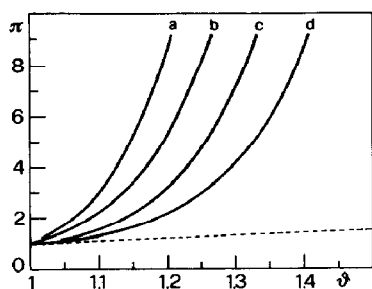


Fig. 3. Dimensionless pressure  $\pi = P/P_0$  against the dimensionless temperature  $\vartheta = T/T_0$ , for different values of the initial temperature  $T_0$ . (a)  $T_0 = 90^\circ\text{C}$ ; (b)  $T_0 = 70^\circ\text{C}$ ; (c)  $T_0 = 50^\circ\text{C}$ ; (d)  $T_0 = 30^\circ\text{C}$ .

All the curves start with a quasi-zero derivative, which dramatically increases just before the “explosion time”. No significant effect of the reactant consumption is observed in the case examined, because of the rather high reactivity of the system considered.

This sharp increase of temperature allows the accurate evaluation of the explosion delay  $t_E$ . On the other hand, its evident drawback is the difficulty in early detecting the runaway from temperature measurements. In fact, the most up-to-date detection systems are rather complex devices, which use the computed values of the first and the second time derivative of the temperature [11,12].

On increasing the initial temperature, the dimensionless explosion delay increases. The anomaly is only apparent, and depends on the values assumed by the characteristic time (eqn. 23), which is a strongly decreasing function of  $T_0$ . As a consequence, the dimensional explosion delay decreases on increasing  $T_0$  according to the expected logarithmic law, as shown in Fig. 2. Moreover, the plotted data show that the dimensional explosion delay is a decreasing function



of the initial concentration of the reactant, expressed by the dimensionless group  $\chi_R$  (eqn. 21).

From the data plotted in Fig. 2 the *safe* temperature  $T_F$  can be defined as the temperature which corresponds to explosion delays high enough to allow the standard shut-down operations. This choice is in some respects arbitrary, but a value of  $T_F$  is in any case required to evaluate the performance of the suppression system.

The early detection of the runaway is essential for attaining an effective operation. It can be observed that the exponential dependence of the vapour pressure on temperature makes the relative pressure increase during the runaway much higher than the corresponding temperature increase, as shown by the curves  $\pi(\vartheta)$ , plotted in Fig. 3 for different values of the initial temperature. In particular, the discussed effect appears more notable at the higher values of  $T_0$ , i.e. when the explosion is more severe, because of the smaller values of the explosion delay.

This observation favours a detection procedure based on pressure measurements. In practical applications, however, different criteria (e.g. the sensitivity and reliability of the sensor) determine the choice of the detection system. Here, it appeared more suitable to use the pressure of actuation (instead of the temperature) to define the time of actuation.

The analysis of the performance of the suppression system can now be attempted. In addition to the chemical and physical properties fixed at the values reported in Table 1, suitable values were assigned to the safe temperature ( $T_F = 60^\circ\text{C}$ ), the initial temperature ( $T_0 = 80^\circ\text{C}$ ), and the inlet temperature of the suppressor ( $T_S = 10^\circ\text{C}$ ). The chosen safe temperature gives an explosion delay (more than two hours) much greater than that corresponding to the initial temperature (about 15 minutes). The reduction of the concentration of the reactant, which occurs during the runaway, gives a further safety margin.

The first tests were performed using the value of the filling ratio reported by Booth et al. (i.e.  $F = F_0 = 0.824$ ). The suppression system appeared unable to protect the reactor, whatever the values assigned to the pressure of actuation and to the flow rate of suppressor. In fact, the volume available in the reactor for the assigned value of  $F$  is too small to hold the mass of suppressor necessary to decrease the temperature from the initial to the safe value.

The tests carried out for smaller values of the filling ratio showed that the effect of  $\pi_A$  and  $\dot{\mu}_S$  is much smaller than the effect of  $F$ . In fact, the pressure of actuation determines the temperature attained by the system at  $t = t_A$ , but its effect is small because, in the range examined, it always results  $T_A - T_0 \ll T_0 - T_S$ . On the other hand, the flow rate of suppressor only determines the length of the suppression period, with only a negligible influence on the total mass of suppressor discharged.

On the contrary, the runaway is dramatically affected by the filling ratio. On decreasing  $F$ , two different behaviours are observed, as shown in Fig. 4. Curve

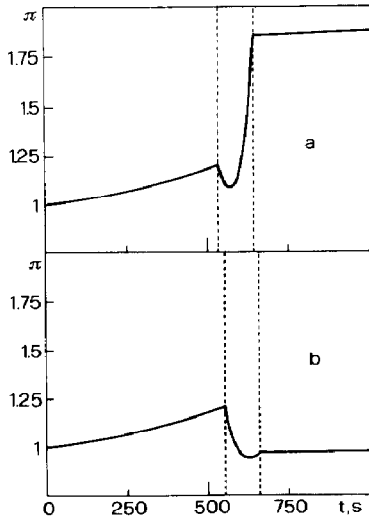


Fig. 4. Dimensionless pressure  $\pi = P/P_0$  during the runaway for two values of the filling ratio  $F$ . (a)  $F = 0.8F_0$ ; (b)  $F = 0.6F_0$ .

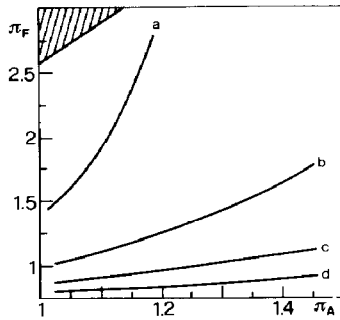


Fig. 5. Maximum dimensionless pressure  $\pi_F$  against the dimensionless pressure of actuation  $\pi_A$  for different values of the filling ratio  $F$ . (a)  $F = 0.7$ ; (b)  $F = 0.6$ ; (c)  $F = 0.5$ ; (d)  $F = 0.4$

(a) refers to  $F = 0.8 F_0$ . The suppressor produces an almost linear decrease of temperature (not shown) and a non-linear decrease of pressure, explained by the decrease of the vapour pressure. Successively, the pressure increases again, because of the decrease of the volume available for the gaseous phase. The maximum pressure, attained at  $t = t_F$ , is noticeably greater than  $\pi_A$ .

At lower values of  $F$  (i.e.  $F = 0.6 F_0$ , curve b), the pressure monotonically decreases during the suppression period, resulting in  $\pi_F < \pi_A$ . In both cases, the “maximum pressure” is almost independent of the suppressor flow rate and only slightly affected by the pressure of actuation.

The maximum pressure represents a simple measure of the effectiveness of the suppression system. Therefore, the computed values of  $\pi_F$  were plotted as a function of  $\pi_A$ , for different values of  $F$  (Fig. 5). The data show that the

maximum pressure increases on increasing the pressure of actuation; moreover, the greater the value of  $F$ , the greater the effect of  $\pi_A$ . In the high left corner, the dashed zone indicates the dominion in which no protection is possible, because the suppressor is unable to reduce the temperature down to the safe value, irrespective of the pair  $\pi_A, F$ .

## Conclusions

The comparison between these results and the performance of a venting system [10] shows that the proposed system requires smaller values of both  $\pi_A$  and  $F$ . However, this work demonstrates that a safety device based on containment and *in situ* inerting is feasible for the protection of chemical reactors against runaway reactions, at least in the case examined (vapour pressure tempered and non-gassy systems). The proposed approach could be extended to evaluate the feasibility of such devices in different cases.

Still within the limits of the simplified analysis proposed, it clearly appears that two main factors determine the effectiveness of this device, namely the early detection of the runaway and the allowance for a suitable gaseous freeboard, i.e. the use of filling ratios smaller than usual.

The early detection of the runaway can be accomplished through the development of suitable software for the real-time analysis of measured data on the state of the system, whereas the allowance for a larger freeboard essentially results in an increase of the costs. However, these costs must be compared with the costs of a complete and reliable blow-down system.

Such an analysis is beyond the scope of this paper but the discussed results clearly show that the economic feasibility of the proposed system deserves further consideration, particularly in the case of toxic and/or flammable effluents.

## References

- 1 H.G. Fisher, DIERS research program on emergency relief systems, Chem. Eng. Prog., 81 (1985) 33-36.
- 2 L. Friedel and S. Purps, Model and design methods for sudden de-pressurization of gas/liquid-vapor reaction systems, Int. Chem. Eng., 26 (1986) 396-407.
- 3 A.K. Fauske, Scale-up for safety relief of runaway reactions, Plant/Operations Prog., 3 (1984) 7-11.
- 4 A.K. Fauske, Generalized vent sizing nomogram for runaway chemical reactors, Plant/Operations Prog., 3 (1984) 213-215.
- 5 J.E. Huff, Emergency venting requirements, Plant/Operations Prog., 1 (1982) 211-229.
- 6 J.C. Leung, Simplified vent sizing equations for emergency relief requirements in reactors and storage vessels, AIChE J., 32 (1986) 1622-1634.
- 7 J.C. Leung, Overpressure during emergency relief venting in bubbly and churn-turbulent flow, AIChE J., 33 (1987) 952-958.
- 8 J.C. Leung and H.K. Fauske, Runaway systems characterization and vent sizing based on DIERS methodology, Plant/Operations Prog., 6 (1987) 77-83.

- 9 S.S. Gossel, Design and sizing of knock-out drums/catchtanks for reactor emergency relief systems, *Plant/Operations Prog.*, 5 (1986) 129-135.
- 10 A.D. Booth, M. Karmarkar, K. Knight and R.C.L. Potter, Design of emergency venting systems for phenolic resin reactors, Part I and II, *Trans. Inst. Chem. Eng.*, 58 (1980) 75-90.
- 11 L. Hub, J.D. Jones, Early on-line detection of exothermic reactions, *Plant/Operations Prog.*, 5 (1986) 221-224.
- 12 J.A. Noronha, Use of DIERS bench-scale apparatus for restabilization and venting runaway reactions, 5th Int. Symposium on Loss Prevention and Safety Promotion in the Process Industries, Cannes (F), paper no. 41 (1986).