

Emergency pressure relief calculations using the computer package: RELIEF

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Received 4 August 1994; accepted 5 December 1994

Abstract

The computer package RELIEF has been specifically designed to model the transient one-dimensional fluid dynamic behaviour of multicomponent chemically reacting mixtures in batch-type chemical reactors or storage vessels. The physical model that describes the above phenomena is coupled to a sophisticated input/output processor that creates an environment in which a problem can be easily set up and executed and the results investigated. A complete “stand alone” package is thus created in which much attention has been devoted to minimising the input requirements and model running time. This has made the package an ideal tool for performing parametric studies of relief scenarios, and highlighting the key phenomena that control the process being studied. A number of emergency pressure relief calculations are presented that illustrate the capabilities of RELIEF.

Keywords: Runaway reaction; Emergency pressure relief; Two phase; Scaling; Computer simulation

1. Introduction

An uncontrolled thermal runaway reaction in a batch-type reactor or storage vessel is one of the accidental events still occurring frequently in the chemical industry. These events result from many causes including operator error, stirrer failure, reactant accumulation, external fire loading, segregation of components, spontaneous decomposition, etc.

Often coupled to this is a lack of detailed knowledge concerning the physical properties, chemical kinetics and information regarding unwanted side-reactions under runaway conditions. The consequences of such events can be benign (but still costly in terms of lost production) when the products are safely vented to a catch tank

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or similar device, or can in certain circumstances be disastrous in terms of the effect on the environment when the products are released to the atmosphere. One only has to remember Bhopal and Seveso.

Public concern has led industry to address seriously the environmental issues, and currently industry is investing 25–30% of the total process cost in achieving this. In an existing plant, retro-fitting equipment is frequently performed and since the capital cost of such equipment is high, it is very important that it is sized correctly. In a new plant there is a growing tendency to design out the runaway potential, but this is not always possible and goes against the trend of manufacturing multipurpose equipment.

There exists a genuine requirement for an engineering tool that is quick running and easy to use, requesting the minimum of input data, such that, at an early stage in a process design, the various safety options can be modelled, assessed and costed.

In view of the importance, the area of runaway reactions and emergency pressure relief has received much attention in recent years. A significant contribution in this area has been the work performed in the DIERS project under the auspices of the American Institute of Chemical Engineers, and latterly the “Industrial Hazards” programme of the JRC.

2. Reactor relief phenomena

The situation considered can be generalised as being a vessel containing a multi-component liquid mixture in which a chemical reaction occurs. If the generation of reaction heat in this mixture exceeds the heat removal rate of the control system, a thermal runaway process will occur which is strongly enhanced by the Arrhenius-type temperature dependency of reaction rate. When operational measures can no longer control the situation, the temperature will rise to levels where the volatile components of the liquid reactant mixture will start to evaporate, and in addition, gas can be produced as a result of a decomposition reaction. This volume production leads to an increase of system pressure and, in order to prevent over-pressurisation of the vessel, it is necessary to discharge the fluid mixture from the vessel at a sufficient rate.

A computational model must therefore describe the chemical conversion, the heat and mass transfer between the liquid and vapour phases, the distribution of components in both phases, the two-phase fluid dynamic behaviour and the interactions between these processes.

3. Two-phase fluid dynamic behaviour

During the progress of a runaway reaction, there is a volumetric source in the liquid phase resulting from evaporation and/or reaction gas production. The bubbles of vapour or gas generated within the liquid will rise through the liquid and disengage at the liquid surface. If the rise velocity is sufficiently high droplet entrainment can occur.

The bubbles during their residence in the liquid occupy a volume and so cause the liquid level to rise or “swell”.

When the set pressure of the safety device is reached and the vessel relieves, the pressure falls and the evaporation or “flashing” increases markedly. This causes the liquid level, or more precisely the “two-phase mixture level”, to rise further and, if this level reaches the vent position, two-phase venting will occur. The depressurisation rate of a system is directly proportional to the *volume* flow rate exiting the system, and since the latter, under critical flow conditions, is inversely proportional to the mixture density at the vent line entrance, the capacity to reduce the system pressure by venting is strongly reduced when the mixture level reaches the vent position. Typically, relief systems that have been designed for two-phase flow conditions will be 2–10 times larger than those designed for single-phase flow. If the volume production rate due to evaporation and gas production is greater than the vented volume flow rate the system pressure will increase. Therefore, the ability to describe the motion of the two-phase mixture level is one of the most important aspects of reactor relief modelling.

In RELIEF the vessel is discretised in the vertical direction into control volumes for which conservation laws pertaining to the phases are applied. The description of the relative motion of the phases is made with a mixture momentum equation and an algebraic drift-flux model. The application of the drift-flux model is justified

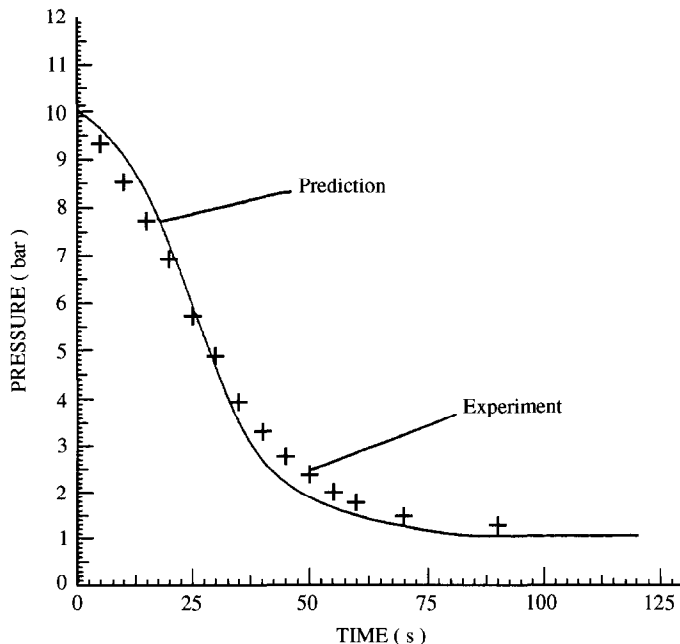


Fig. 1. DIERS T8a water blowdown test pressure history.

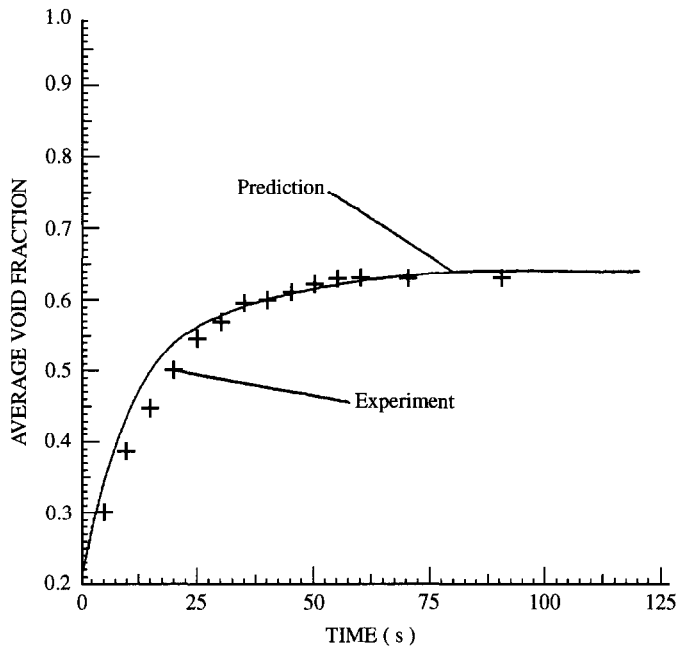


Fig. 2. DIERS T8a water blowdown test vessel void fraction history.

as the acceleration and wall friction terms in the momentum equation are negligible when compared to the buoyancy term. The model in RELIEF describes bubbly flow, churn turbulent flow and droplet flow by a continuously varying function of drift-flux and void fraction; the foundations of this model are given in Refs. [1, 2]. Figs. 1 and 2 show the predictions of pressure and average vessel void fraction for one of the DIERS large scale water blowdown experiments [3].

4. Chemical systems

Chemical reactions are normally the cause of a pressure increase in closed vessels. Even endothermic reactions can cause a pressure increase if the reaction products are gases, or liquids which are more volatile than the reactants. Exothermic reactions are potentially more dangerous, as in addition they raise the temperature of the reactants and hence accelerate the chemical reaction. At present in RELIEF chemical reaction is limited to the liquid phase where up to ten irreversible reactions of arbitrary order can be modelled.

Often in the literature distinction is made between the mechanism of this pressure rise so that simplifications can be made to the mathematical treatment of relief system

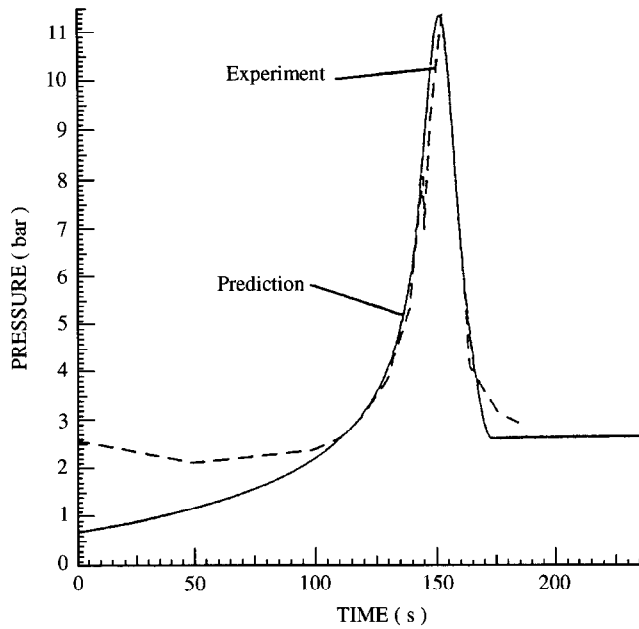


Fig. 3. Acetic anhydride/methanol runaway pressure history.

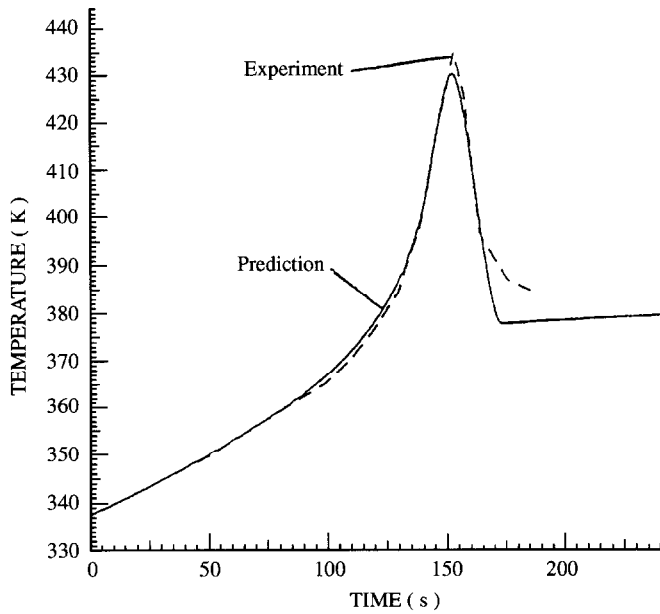


Fig. 4. Acetic anhydride/methanol runaway temperature history.

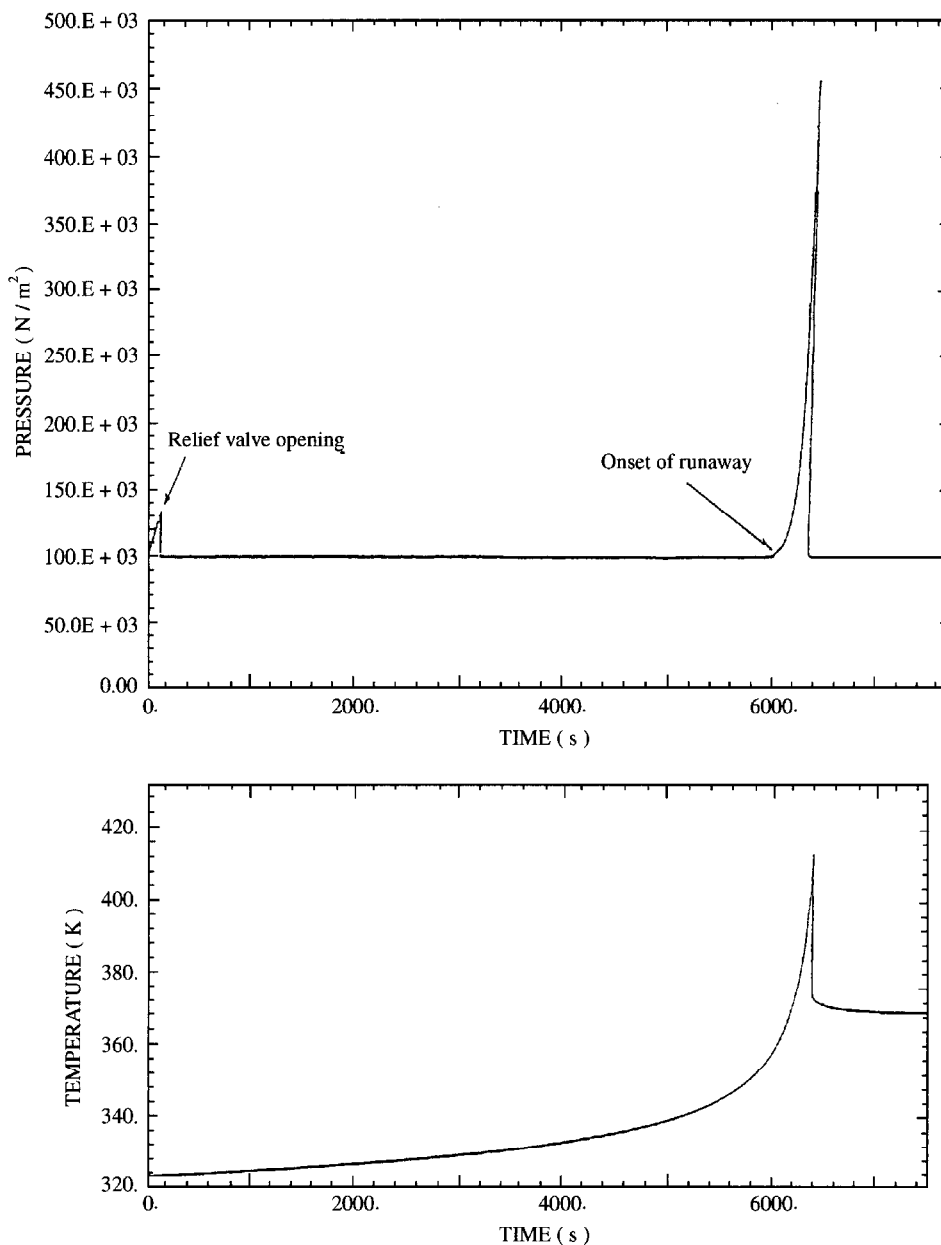


Fig. 5. Hydrogen peroxide decomposition: Pressure, temperature and mass fraction histories.

sizing. The following distinctions are usually made:

(a) "Vapour pressure" or "tempered" systems, in which the pressure generated by the reaction is due to the increasing vapour pressure of the reactants, products and/or inert solvent as the temperature rises.

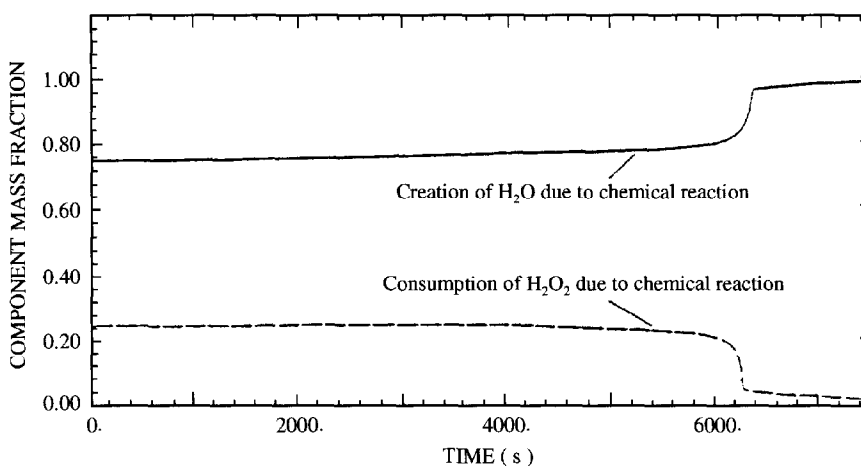


Fig. 5. Continued.

(b) “Gassy” systems, in which the pressure is due to the production of a permanent gas by the reaction.

(c) “Hybrid” systems, in which the pressure rise is due to both an increase in vapour pressure and permanent gas generation.

For such classifications a number of analytical tools and formulae can be used to calculate the vent size for a particular overpressure. These “hand calculation” methods usually treat the vessel as a single node having uniform properties. The obvious difficulty arises when this assumption is not valid and when it is not known a priori what type of system is expected. RELIEF does not suffer from these restrictions and the type of reaction system can be deduced from the results.

Figs. 3 and 4 illustrate the runaway of a vapour pressure system. The reaction considered is the esterification of acetic anhydride and methanol with the experimental data provided by [4]. The close coupling between temperature and pressure is clearly seen.

Some of the more difficult problems to be solved are the hybrid systems, since the temperature and pressure effectively become uncoupled due to the production of noncondensable products. Unfortunately, this type of system is very common, as in the runaway phase undesired decomposition reactions often occur. Fig. 5 shows the runaway of an aqueous hydrogen peroxide solution which can be regarded as prototypical of this type of system. The batch size is about 1 t containing 25% mass fraction of hydrogen peroxide. One should note that there is a rather long period of time between the initial upset, leading to the opening of the relief valve, and the major excursion in pressure and temperature, so that for control purposes it would be useless observing only the system pressure.

5. Scaling considerations

The size and aspect ratio of a system has much more influence on the hydrodynamic behaviour than on the chemical behaviour. This is because chemistry is governed by the elementary molecular reactions whereas the hydrodynamics are governed by bubbles and droplets with typical dimensions in the range 1–10 mm. Over this range, bubbles generated within a liquid will rise at a reasonably constant speed [5]; therefore, their residence time will be longer for a tall vessel, leading to an increased level swell, compared to a short vessel. The effect of this is demonstrated by a RELIEF calculation shown in Fig. 6. Two vessels of equal volume but differing aspect ratios (a factor 10) have been modelled in which a vapour pressure runaway reaction (bulk polymerisation) proceeds. In all other respects the calculations are identical. One can see that a pressure excursion occurs in the tall vessel but not in the short one. The increase in the level swell for the tall vessel causes the two-phase mixture level to reach the vent location resulting in two-phase venting and a reduced relief capacity.

A similar calculation is shown in Fig. 7, but instead of a vapour pressure system, a decomposition or hybrid system has been modelled. In this case the trend is exactly the opposite!

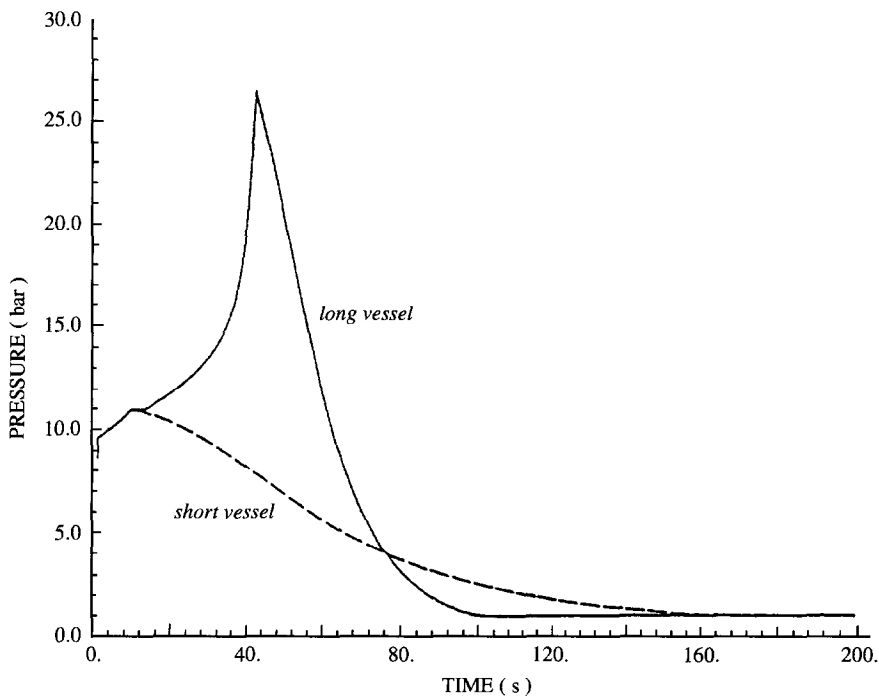


Fig. 6. Influence of vessel height on pressure history: Vapour pressure system (polymerisation).

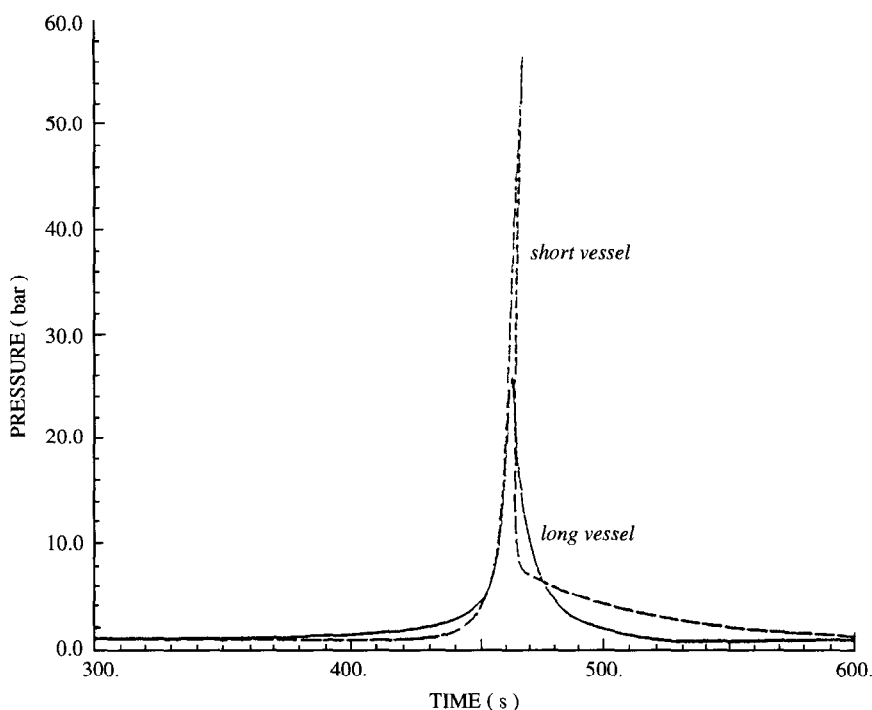


Fig. 7. Influence of vessel height on pressure history: Hybrid system (decomposition).

For this type of system, the pressure response is extremely sensitive to the amount of mass vented early on in the runaway phase. Only with the aid of a dynamic simulation of the runaway can one appreciate some of these differences. This makes the search for simple scaling rules difficult.

6. Design strategies

The flexibility and ease with which RELIEF can be used as a design tool can be illustrated by the following examples. The first considers the addition of a solvent to temper or moderate the runaway in a hybrid system. The system studied is the aqueous solution of hydrogen peroxide. The relief line was sized such that a significant pressure excursion occurred, and then in successive calculations a proportion of the water was substituted with methanol. Figs. 8 and 9 show the pressure and temperature histories in which it can be seen that the effect of adding methanol is not so straightforward. Initially it has a deleterious effect raising the peak pressure, and only when a significant amount of methanol is added is the reaction tempered.

RELIEF has the capability of modelling several vent lines located at any position on the vessel. This enables various design strategies to be studied, such as the operation of multiple staggered relief valves, and combined top and bottom venting.

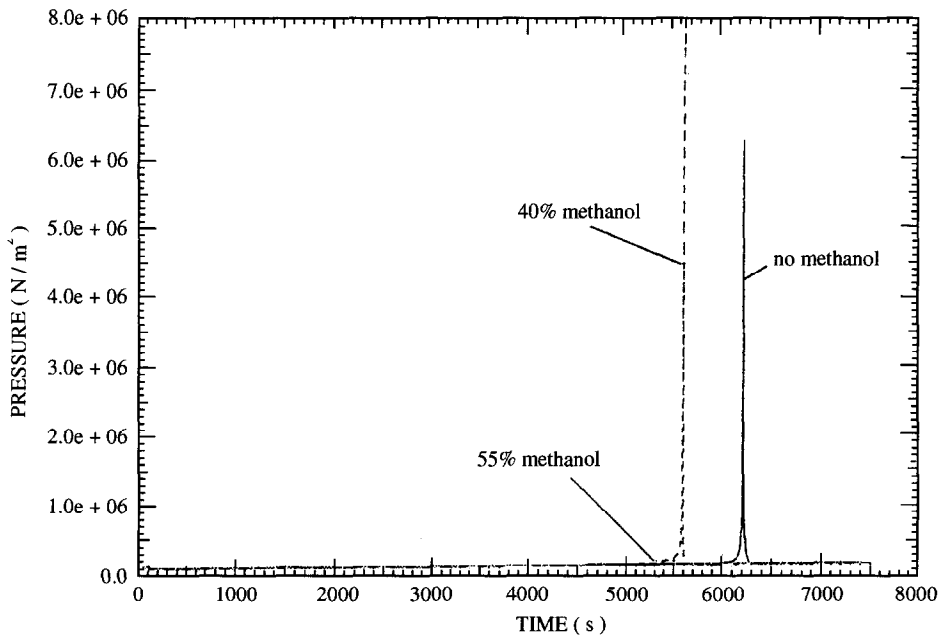


Fig. 8. Effect of methanol as a tempering agent: Pressure history (decomposition reaction).

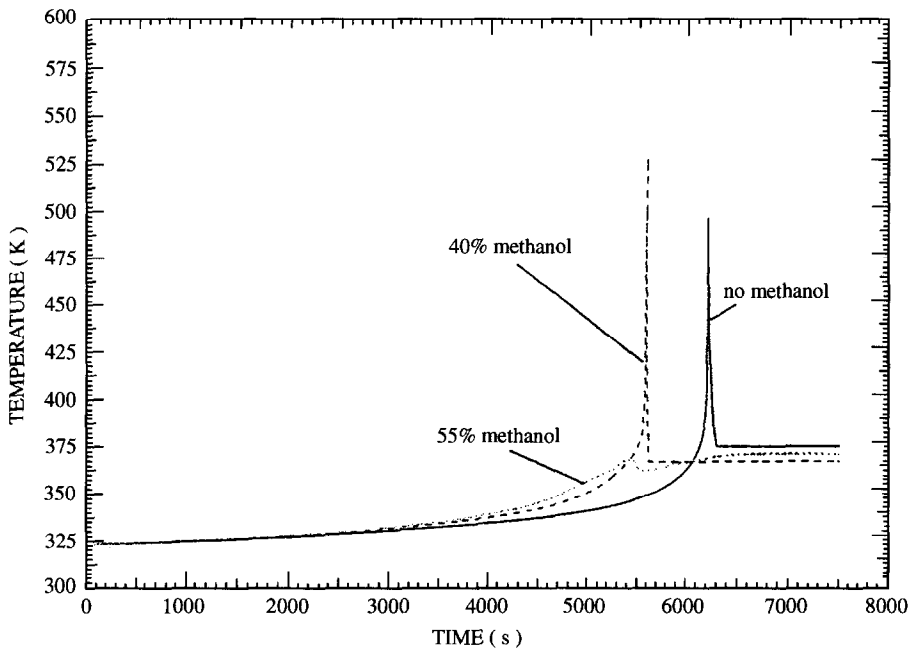


Fig. 9. Effect of methanol as a tempering agent: Temperature history (decomposition reaction).

The second example studies the performance of a combined top and bottom safety relief system, and again the system chosen is an aqueous solution of hydrogen peroxide. Two calculations were made, the first being a simple top venting with a relief line sized as in the above example and the second maintaining the same total vent area as the first calculation but distributed such that half the vent area is at the top and half

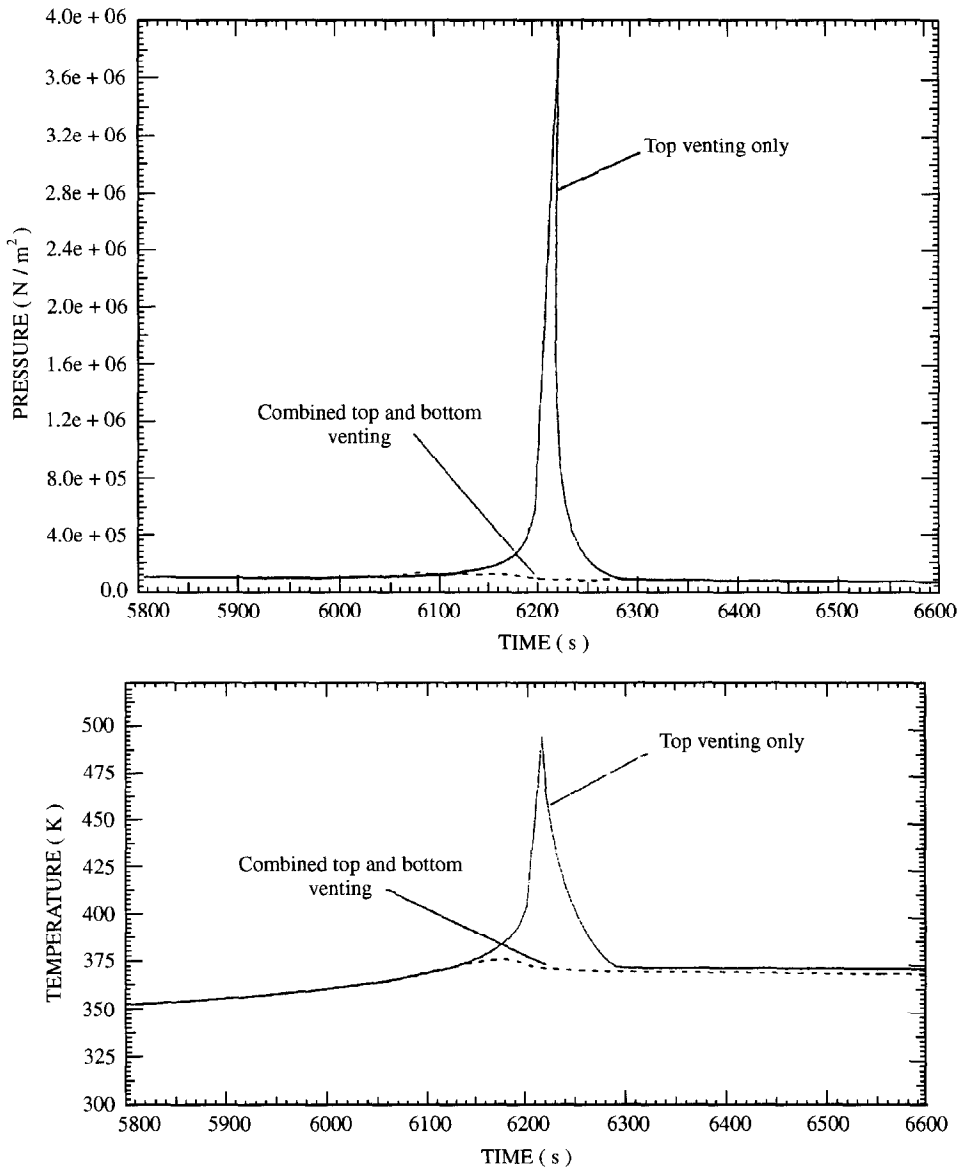


Fig. 10. Hydrogen peroxide decomposition reaction: The effect of combined top and bottom venting.

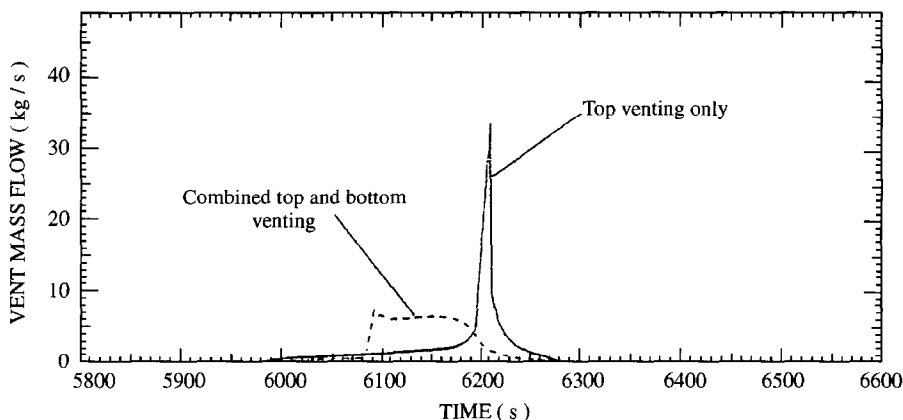


Fig. 10. Continued.

at the bottom. The set pressure for the bottom vent line is given a value 0.15 bar above the set pressure of the top vent line. Fig. 10 shows the pressure, temperature and mass flow rate histories for the two calculations. There appears to be no difference between the two cases up to ≈ 6000 s, but thereafter the results are very different. For the case of top venting the maximum pressure exceeds 60 bar, whereas with combined venting, the peak pressure is limited to the set pressure of the bottom vent, i.e., 1.5 bar. Referring to the mass flow rates, it is clear that bottom venting does not occur until 6100 s into the transient after which time significantly more mass is vented, thus achieving the goal of venting reactant early on in the runaway phase.

A further example could be the determination of the maximum reactor filling that would lead to only single-phase vapour being discharged in the event of a runaway. This strategy would reduce the operational efficiency of the reactor as the reactor may be only half full, but it would significantly reduce the capital cost of the relief system since no expensive separation equipment would be required and the products could be simply routed to a flare stack.

7. Conclusions

Environmental issues concerned with the release of chemicals to the atmosphere are being addressed seriously by the chemical industry. This work accounts for a significant proportion of the total process cost. There appears to be a genuine requirement for an engineering tool that is quick running and easy to use, requesting the minimum of input data, such that at an early stage in a process design various safety options can be modelled, assessed and costed. The computer package RELIEF has been specifically designed to fulfil this need.

In this paper a number of calculations have been presented that highlight the key phenomena associated with runaway reactions and emergency pressure relief. In addition, it has been shown how RELIEF can be used to analyse various relief design

strategies. An attempt has been made to illustrate the complexity of the problem and show that some results are indeed counter-intuitive. The quest to find simplified formulae to describe these processes appears at the very least questionable.

In view of the large capital cost associated with downstream separation equipment and containment vessels, it is important that the safety systems are incorporated into the overall process design at the earliest possible stage.

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