

COMPUTER SIMULATIONS DESCRIBING THE EMERGENCY PRESSURE RELIEF OF HYBRID AND GASSY SYSTEMS

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One of the more challenging problems when considering emergency pressure relief design concerns the type of reaction that produces a non-condensable gas as a reaction product. The temperature and pressure of such systems become effectively decoupled. This paper presents some computations performed with the computer package RELIEF, developed at the JRC establishment of the CEC. Specific attention is focused on "hybrid" and "gassy" reactions and the use of volatile solvents to moderate the runaway.

Key Words: Runaway reactions, emergency relief, two-phase flow, computer simulations

INTRODUCTION

A runaway reaction in a batch type chemical reactor or storage vessel is one of the accidental events which may occur in the chemical industry. The consequences of such an event can be benign (but still costly in terms of lost production) when the products are safely vented to a dump tank or similar device, or can be disastrous in terms of the effect on the environment when the products are released to the atmosphere, as for example in the case of the accidents at Seveso and Bhopal. Hybrid and gassy systems, for example peroxide solutions, pose a particular problem in that they are often unstable, highly energetic and usually react yielding non-condensable decomposition products. This paper studies the thermal runaway of a water / hydrogen peroxide solution which can be thought of as being prototypical of hybrid and gassy systems in general.

An uncontrolled release to the atmosphere usually occurs due to vessel failure, which often results from the fact that the emergency relief system is not correctly sized. Traditionally the emergency relief systems were designed assuming single-phase conditions in the vent line, whereas in reality often two-phase conditions prevail. Compared to relief systems designed to handle single-phase vapour, two-phase flow requires vent sizes that are 2 - 10 times larger. An additional complication arising from two-phase discharge is the requirement to install special equipment to treat the relieved fluids if they are toxic or flammable. This special equipment may consist of knock-out drums, vapour-liquid separators, catch tanks, condensers, etc. Whatever the system the cost of such equipment is not insignificant, therefore it is important to optimise the size of the relief lines and ducting, i.e. they should be large enough to ensure that the peak pressure stays within safe limits during relief, but not too large in order to minimise the amount of relieved fluid to be treated.

In view of this interest, much effort has been expended over the last decade in an attempt to improve the understanding of the basic phenomena associated with emergency relief. For example, the chemical industry has performed many experiments some of which have been described in the open literature, the JRC has a framework programme dealing with "Industrial Hazards", and a major effort has been the work performed in the DIERS (Design Institute for Emergency Relief Systems) project. DIERS consists of a consortium of companies under the auspices of the American Institute of Chemical Engineers and was formed to generate experimental data on large-scale vessels undergoing either runaway reactions or external heating (e.g. by external fires or loss of cooling), and to develop

methods for the safe design of emergency relief systems to handle these events. Significant progress has been made but the knowledge obtained is by no means complete.

This paper will concentrate on what happens within the vessel during emergency relief, and an attempt will be made to highlight the basic phenomena that are present and how they interact and affect the course of the transient. The computer code RELIEF, developed at the JRC, has been used to simulate the runaway and to perform parametric studies. The important aspect of multicomponent, chemically reacting, two-phase critical flow in vent lines has been discussed previously [1], but here attention will be restricted to short vent lines where it is justifiable to neglect the effect of an ongoing chemical reaction in the vent line.

REACTOR RELIEF PHENOMENA

The situation under consideration can be a batch reactor or storage tank containing a multicomponent 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 this situation cannot be controlled by operational measures, the temperature will rise to levels where the volatile components of the liquid reactant mixture 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 reactor vessel it is necessary to discharge the fluid mixture from the vessel at a sufficient rate. For sizing the emergency relief system, required by safety rules, it is necessary to dispose of adequate computation models which must be based on a correct description of the chemical conversion, of mass transfer between liquid and vapour phase, of two-phase fluid dynamics and of the interactions between these processes.

Level Swell

Chemical reactions can be the cause of a rise in pressure in a closed system by increasing the vapour pressure of the system and/or by generating non-condensable gases as reaction or unwanted decomposition products. 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.

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 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.
- (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.
(In fact often hybrid systems are classified as either being "hybrid/tempered" or "hybrid/ non-tempered" systems.)

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. An excellent review of existing vent sizing methods of this type is given by Duxbury and Wilday [2] and more recently by Fisher [3].

When a runaway reaction is in progress there is a volumetric source in the liquid phase resulting from evaporation and/or reaction gas production. The bubbles of vapour and/or gas generated within the liquid tend to rise through the liquid and disengage at the liquid surface. If the rise velocity is sufficiently high then droplet entrainment can occur. The bubbles during their residence in the liquid occupy volume and so cause the liquid level to rise or "swell".

When the set pressure of the safety device is reached and the reactor or storage vessel relieves then the pressure falls and the evaporation or "flashing" increases markedly. This causes the liquid level, or to be more precise 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. 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. In a runaway situation if the volume production rate due to evaporation and/or 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.

Interfacial Momentum Transfer The general area of interfacial momentum transfer in pool systems containing arbitrary fluids and subject to depressurisation is still an open area of research. There is a paucity of experimental data particularly for high viscosity fluids from which realistic models can be developed. The problem reduces to the description of the motion of bubbles within a continuous liquid phase and the motion of droplets within a continuous vapour phase, and how this motion changes with void fraction. In a bubbly liquid in a pool where wall effects are negligible, the friction or drag exerted by the liquid on the bubble surface determines how fast the bubbles rise within the liquid. This frictional force in comparison to the buoyancy force decreases markedly as the bubbles increase in size. As the void fraction increases the rate of slip of the vapour past the liquid increases until the situation arises when the liquid begins to break up into droplets and the vapour becomes the continuous phase. The drag between the droplets and the vapour increases as the droplet size decreases and so the slip decreases. At the extremes of all liquid and all vapour flow the slip must obviously be zero, and at some intermediate void fraction the slip will be a maximum where the bubbles or vapour "packets" have their maximum size.

Phase slip is closely related to phasic momentum transfer, a process usually described in terms of a mixture or drift flux model[4] or a two-fluid model[5].

In the drift flux model the phasic momentum equations are replaced by a mixture momentum equation and the relative velocity between the phases is described by a steady state correlation. Its validity is limited to situations where acceleration and wall friction forces can be neglected.

The two-fluid model uses a separate partial differential equation, averaged over the flow cross section, to describe the motion of each phase.

* The two-phase mixture level separates the region which is predominately liquid (possibly containing vapour bubbles) from the region which is predominately vapour (possibly containing liquid droplets) and is usually defined as the position where there is a discontinuity in the axial void fraction profile

To solve these equations one has to specify a correlation for the interfacial drag force. If a force balance is made on a single bubble it can be shown that[6]:

$$\tau_i = \frac{3}{8} \frac{\alpha_{li} U_s^2 C_d}{r_b} \quad (1)$$

The basic empiricism of the two-fluid model enters in determining the values of C_d and r_b .

In the particular case of pool boiling or flashing in large diameter vessels (such as batch reactors or storage tanks) the velocities are low and the temporal, acceleration and convective terms in the momentum equations can be neglected as too can the terms related to wall friction and momentum transfer due to phase change. Thus in this case there is little to choose between the drift flux approach and the two-fluid model except that the drift flux model generally requires less computing time.

For this reason the drift flux approach has been adopted in RELIEF and the variation of the phasic velocity difference as a function of void fraction is given below,

$$U_v - U_l = U_{pool} \cdot \frac{\alpha^m (1 - \alpha)^n}{\alpha_{max}^m (1 - \alpha_{max})^n} \quad (2)$$

where α_{max} is the void fraction which gives the term $\alpha^m (1 - \alpha)^n$ its maximum value.

The denominator is a scaling factor which ensures that the maximum value of the slip is given by U_{pool} irrespective of the value of void fraction at which it occurs. The coefficients m and n describe bubbly flow and droplet flow respectively, they have been fitted to experimental data. U_{pool} contains the physical property group $\left[\frac{g \Delta \rho}{\rho_l^2} \right]^{1/4}$ and can be thought of as a characteristic bubble velocity representative of a pool situation.

With the constant 1.53, U_{pool} is identical to the churn-turbulent regime as defined by Zuber [7]. This definition has much success in describing drift flux experiments where gas is bubbled through a liquid column in reasonably small diameter tubes, say up to diameters of 10 cm. However, there is a general awareness that this value significantly underpredicts the rise velocity in flashing pool situations. For a more detailed discussion reference should be made to the following articles by, Filimonov[8], Styirkovich [9], Gardner [10], and Kataoka and Ishii [11].

Multicomponent Equilibrium

Unlike a single component fluid where the saturation pressure is a pure function of the system temperature, the equilibrium pressure of a multicomponent mixture is a function of the system temperature and the distribution of the components over the liquid and vapour phases. Here it is assumed that the vapour is a mixture of ideal gases and the liquid behaves as an ideal mixture. The distribution of components over the liquid phase and gas phase then may be evaluated applying Raoult's law and Dalton's law.

The equilibrium pressure of a multicomponent mixture is given by the sum of the component partial pressures.

$$\sum_i P_i = P \quad (3)$$

According to Raoult's law the partial pressure of component (i) is given by the product of the component liquid mole fraction x_i and the saturation pressure $p_{sat(i)}$ of the pure component (i) at the system temperature.

$$p_i = p_{sat(i)} x_i \quad (4)$$

Dalton's law implies that the partial pressure of component (i) is equal to the product of the gas phase mole fraction y_i and the system pressure.

$$p_i = p y_i \quad (5)$$

Thus the distribution of component (i) over the liquid and gas phases is given by:

$$\frac{y_i}{x_i} = \frac{p_{sat(i)}}{p} = K_i \quad (6)$$

where K_i is known as the phase equilibrium ratio. For non-ideal liquid mixtures Raoult's law can be modified with the addition of the activity coefficient γ_i of component (i).

$$p_i = p_{sat(i)} x_i \gamma_i \quad (7)$$

Chemical Reaction

An ongoing chemical reaction is a potential source of both volume (due to the generation of new products) and heat. The reaction under consideration is the decomposition of hydrogen peroxide, symbolised by the stoichiometric equation,



The instantaneous conversion rate of reactant, hydrogen peroxide, is described by the first order reaction,

$$r_{H_2O_2} = \frac{d[C_{H_2O_2}]}{dt} = k_o [C_{H_2O_2}] \exp(-E/RT) \quad (9)$$

where: k_o is an empirical factor called the frequency factor, $[C_{H_2O_2}]$ is the concentration of hydrogen peroxide, E is the activation energy, R is the gas constant and T is the absolute temperature. The heat source for the reaction is given by the enthalpy change of the reaction or from the differences in the heats of formation of the reactants and products.

The frequency factor, activation energy and heat of reaction are normally obtained from detailed calorimetric experiments.

MODELLING PRINCIPLES

In modelling the in-vessel fluid behaviour an attempt is made to separate as far as possible the physical, physico-chemical and thermokinetic phenomena associated with the multicomponent phase-equilibrium and with the exothermic liquid phase chemical reaction from the phenomena pertaining to the two-phase fluid dynamics. The rate of vessel depressurisation and the rate at which fluid is discharged from the vessel depend on the fluid dynamic phenomena in the vent line and on the two-phase flow behaviour of the multicomponent

mixture inside the vessel. Both phenomena are modelled but in this paper major attention is given to the multicomponent two-phase fluid behaviour in the vessel because the vent mass flow rates depend strongly on fluid dynamic conditions at the entrance to the vent line. In the illustrative calculations shown later a simplified critical flow model has been selected to compute the mass flow through the vent line, taking the stagnation pressure and fluid mixture density as the prime governing parameters.

The following hypotheses and assumptions are presently made in the vessel model:

- chemical reaction limited to the liquid phase
- miscibility of all components in the liquid phase
- uniformity of pressure over the flow cross section
- the wall friction and acceleration terms in the momentum description can be neglected
- the kinetic energy terms in the energy equations can be neglected
- axial conduction and axial mass diffusion in the fluid can be neglected
- thermal equilibrium between liquid and vapour phases (no superheat at onset of the depressurisation process)
- distribution of components between phases governed by ideal gas behaviour (Dalton's law) and on ideal liquid solution behaviour (Raoult's law)

It is worth pointing out that most of the above assumptions do not represent limitations of the analysis. Their elimination however requires specification of additional relations containing parameters that have to be determined experimentally (e.g. in case of non-equilibrium, interphase areas and interphase transfer coefficients, for non-ideal liquid mixtures activity coefficients etc.).

ILLUSTRATIVE CALCULATIONS

System Considered

The scenario considered is that proposed by the DIERS group for a recent calculational round robin design exercise [12]. The problem was to recommend an ideal area for venting a runaway H_2O_2 solution that would limit the pressure rise to the design maximum pressure of the vessel. Venting was assumed to be direct to the atmosphere through a vent line of negligible length. The reactor vessel was a vertical cylinder having a diameter of 1 m and length 1.5 m. Wall heat capacity effects were assumed to be negligible. The maximum design pressure of the vessel was 4.45 bar, and the relief valve set pressure was 1.345 bar. The vessel was assumed to be filled initially to about 80% which corresponded to an initial mass of 907kg. The Fe-contaminated hydrogen peroxide / water solution had a composition by weight of 25% H_2O_2 75% H_2O , and the runaway was assumed to start at 50 C. The chemical conversion was assumed to obey the following relation:

$$\frac{d[C_{H_2O_2}]}{dt} = 1.5 \times 10^{12} [C_{H_2O_2}] \exp \left[-\frac{25500}{1.987T(K)} \right] \quad (10)$$

and the heat of reaction was given by:

$$\Delta H_r \approx 2.79 \times 10^6 \quad \text{J/kg } H_2O_2$$

Results and Discussion

DIERS Round Robin Exercise Calculations have been performed with RELIEF in which the relief valve area was systematically varied such that a curve of maximum pressure (or overpressure defined as: $\{(p_{max} - p_{set})/p_{set}\}$) against relief valve area could be drawn. This dependency is shown in figure 1. The shape of the curve should be noted which flattens as the relief area is reduced. This means that the maximum system pressure is very sensitive to changes in area in this region. To limit the pressure rise to 4.45 bar, an overpressure of about 230%, a relief valve area of 47.78 cm² or a diameter of 7.8 cm has to be specified.

Figure 2 shows the total mass vented as a function of vent area. The curve indicates that the same mass can be vented for two different valve areas. This will be discussed in detail later, but it is the first indication that simply a measure of the total mass vented in an experimental study using peroxide solutions (or in fact any reaction where non-condensable products are formed) is insufficient to characterise the transient, and a mass flow rate measurement is essential. It is purely coincidental that the vent area (44.78 cm²) that limits the peak pressure to the design maximum pressure gives the maximum amount of mass vented.

Looking now in more detail at the transient behaviour with this vent area we see in figure 3 the pressure, temperature and concentration of hydrogen peroxide as a function of time. The system is characterised by an early pressure increase due to oxygen being produced by the decomposition of hydrogen peroxide; the temperature of the liquid increases as the heat of reaction is absorbed by sensible heating of the liquid. Then at some point the relief valve set pressure is reached and the relief valve opens. Because the liquid mixture is "subcooled" no significant flashing occurs and primarily oxygen is vented. For a long period of time following the opening of the relief valve the flow in the vent line remains single phase. The valve area is sufficiently large such that it allows all the oxygen produced to be vented and the vessel pressure remains close to ambient. However, the temperature and hence the generation of oxygen continues to increase and during this period the temperature and pressure of the system are effectively decoupled. After some 6000 seconds (marked onset of runaway) volume production by vapour generation becomes sufficiently large to cause the two-phase mixture level to swell to the top of the vessel. This leads to two-phase flow in the vent line and a rapid increase in vessel pressure. The subsequent pressure response is a result of a balance between the volume generation (due to the ongoing decomposition of hydrogen peroxide) and the volume flow rate exiting the vessel through the vent line. Note at the end of the transient not all the hydrogen peroxide has been consumed.

In figure 4 the system mass is displayed as a function of time and it shows that the majority of mass is lost during the two-phase venting phase.

Figure 5 shows the time variation of the relative gas mass fractions, defined as the ratio of the component gas mass to the total mass of the gaseous phase. For the early part of the transient the vapour phase is primarily made up of oxygen. The water vapour content steadily increases due to the increasing temperature of the liquid mixture. After about 5500 seconds the amount of water vapour in the system increases dramatically and at about 6050 there is more water vapour than oxygen. At this time the vessel pressure has not really begun to rise and is still below the original set pressure of the safety valve. The subsequent pressure increase is primarily due to boiling of the water; there is even some hydrogen peroxide vapour formed in this period. Therefore, this transient should be classified as a "hybrid" system which is not at all obvious from the pressure and temperature curves.

Sensitivity Calculations and Combined Top and Bottom Venting The question arises, if it is just the chemical reaction that classifies the system as being tempered, gassy or hybrid, or whether it is a result of the transient and hence depends on the relief valve area. To answer this question two further calculations were performed that had different valve areas but had the same total mass vented. Referring to figure 2 additional calculations were performed

with vent line diameters of 6.3 cm and 8.6 cm, which corresponds to a vented mass of 745 kg. Figure 6 shows the pressure, temperature and hydrogen peroxide concentrations. Even though the vented mass is identical the transients are completely different. With the smaller vent area there is a very strong runaway with the pressure and temperature being limited by the complete consumption of the hydrogen peroxide, whereas with a slightly larger vent area practically no runaway occurs and a significant fraction of hydrogen peroxide remains at the end of the transient.

The key to understanding the differences between the two cases is found in the mass inventory histories (figure 7), and the corresponding mass flow rates (figure 8). With the larger vent area more mass is vented early in the runaway. This vented mass contains a proportion of hydrogen peroxide and so the amount of hydrogen peroxide left within the vessel at this time is less for the case with the larger vent area. This has a feedback on the temperature rise rate and limits the runaway. At about 6100 seconds this mass difference between the two cases is about 50 kg, of which 7.5 kg is hydrogen peroxide; (this represents about 3% or 4% of the hydrogen peroxide inventory). It appears therefore, that the course of the transient is extremely sensitive to the amount of hydrogen peroxide that is vented early on in the runaway phase. For this reason it is important to perform parametric studies of the complete transient. It should be noted that all the simple vent size formulae take no account of any loss of reactant due to venting and this can in many cases yield unrealistically conservative vent sizes.

Figures 9 and 10 show the relative gas mass fractions for the two cases. The transient corresponding to the smaller vent area (figure 9) is more like a gassy system with the vapour phase always being rich in oxygen. Conversely, for the larger vent area (figure 10) the transient is more characteristic of a hybrid system.

The calculations illustrate the importance of the early venting of mass during the runaway phase of the transient. This could be achieved quite effectively by having a combined top and bottom venting of the system.

To illustrate this a comparative calculation has been performed with a combined top and bottom venting. The total vent area for this case was chosen to be the same as for top venting only with a vent diameter of 6.3cm; this gave top and bottom vent diameters of 4.45cm. The set pressure for the top vent was kept at 1.345 bar, but the relief pressure for the bottom vent was set just a little higher at 1.5 bar; in all other respects the two calculations were identical. Figure 11 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 seconds 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, ie 1.5 bar. Referring to the mass flow rates it is clear that bottom venting does not occur until 6100 seconds into the transient after which time significantly more mass is vented thus achieving the goal of venting reactant early on in the runaway phase. Of course this does not entirely solve the problem because the reactant is just transferred to some downstream location where a subsequent runaway could occur, but there it would be much more feasible to control a runaway through quenching etc.

This example illustrates the ease with which an interactive computer model can be used to study various relief design strategies.

The use of Solvents to Temper the System The flexibility and value of RELIEF as a design tool is further demonstrated by the study of the use of a volatile solvent to moderate a runaway reaction. The system is based on the previous example, ie top venting with a vent diameter of 6.3cm, but a proportion of the initial water content is substituted by the more volatile solvent methanol. Figure 12 shows the pressure histories with various initial water/methanol compositions, and figure 13 shows the locus of peak pressure as a function of initial methanol concentration. What is surprising at first is that the addition of methanol initially increases the peak pressure and only when the majority of dilutant is methanol does it have a tempering effect on the system. The explanation for this lies

in the relative magnitudes of the specific heat and latent heat of evaporation of water and methanol, and one has to examine in detail the complete transient to fully understand this behaviour. Figure 14 shows the temperature histories of the case with no methanol, the case where the initial methanol concentration gave the maximum peak pressure ($\approx 40\%$) and the case where the methanol had a significant tempering effect ($\approx 55\%$).

CONCLUSIONS

The runaway reaction involving the decomposition of hydrogen peroxide has been studied. This system can be considered as being prototypical of peroxide solutions in general and many of the conclusions directly apply to "gassy" and "hybrid" systems. These systems can be characterised by a rather long period of time between the opening of the relief valve and the onset of the runaway, typically some hours. During this period the temperature and pressure are decoupled with the pressure remaining close to the ambient pressure but the temperature continually increasing. It has been shown that the system response is extremely sensitive to the amount of mass that is vented early on in the runaway phase. The final mass vented is not a good parameter to characterise the runaway. For these types of systems a combined top and bottom venting would seem more appropriate.

The validity of the simple vent size formulae is questionable for these systems as they could yield unrealistically conservative vent sizes. This has important economic consequences when downstream equipment has to be sized.

It appears difficult to classify the system *a priori* as being gassy or hybrid as the response is not only dependent on the chemical reaction but also on the vent area.

The use of solvents which have the potential to temper a runaway has been studied and it has been shown that the effect is far from straightforward; certain concentrations have a deleterious effect raising the peak pressure, whereas other higher concentrations quench the reaction.

For these reasons the use of computer simulations of the complete transient response of the system is regarded as a necessary complement to experimental calorimetric measurements in order to understand the runaway reaction and assess the potential risk.

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NOMENCLATURE

<i>C</i>	Concentration	kgm^{-3}
<i>C_d</i>	drag coefficient	
<i>c_p</i>	specific heat at constant pressure	$\text{Jkg}^{-1}\text{K}^{-1}$
<i>E</i>	activation energy	Jkmol^{-1}
<i>g</i>	acceleration due to gravity	ms^{-2}
<i>H_r</i>	heat of reaction	Jkg^{-1}
<i>h</i>	enthalpy	Jkg^{-1}
<i>K</i>	phase equilibrium ratio	
<i>k_o</i>	frequency factor	
<i>p</i>	pressure	Nm^{-2}
<i>R</i>	gas constant	$\text{Jkmol}^{-1}\text{K}^{-1}$
<i>r</i>	component mass production rate per unit of phase volume	$\text{kgm}^{-3}\text{s}^{-1}$
<i>r_b</i>	bubble radius	m
<i>T</i>	absolute temperature	K
<i>U</i>	velocity	ms^{-1}
<i>U_r</i>	relative phasic velocity	ms^{-1}
<i>x</i>	component liquid mole fraction	kmol/kmol
<i>y</i>	component vapour mole fraction	kmol/kmol

Greek symbols

α	vapour volume fraction	m^3/m^3
ρ	density	kgm^{-3}
σ	surface tension	Nm^{-1}
τ_i	interfacial drag force	$\text{kgm}^{-2}\text{s}^{-2}$
γ	activity coefficient	

Subscripts

<i>i</i>	component
<i>l</i>	liquid phase
<i>v</i>	vapour phase
<i>sat</i>	saturated

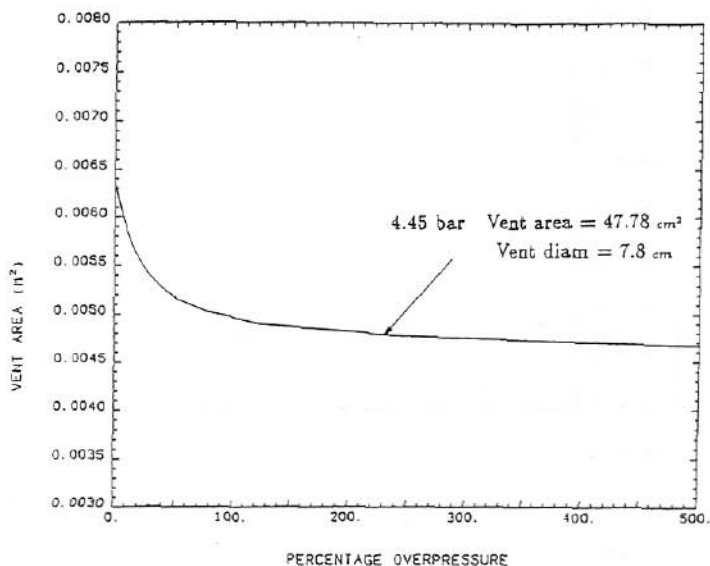


Fig 1. Vent area against overpressure for a hydrogen peroxide decomposition reaction

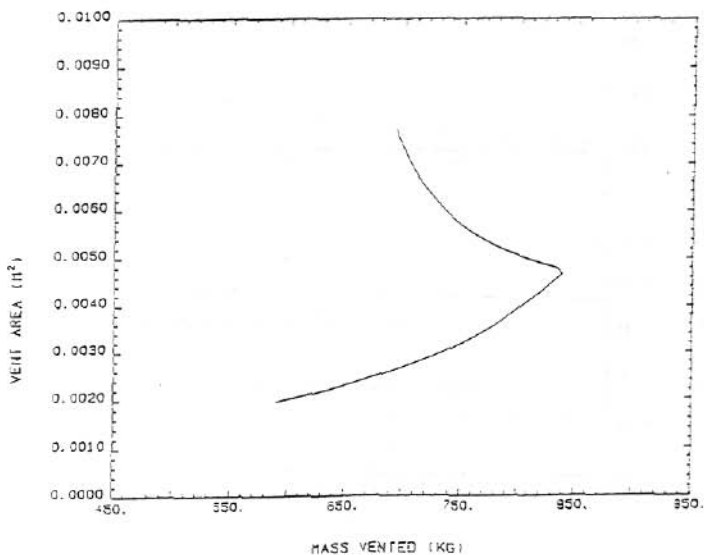


Fig 2. Vented mass as a function of vent area

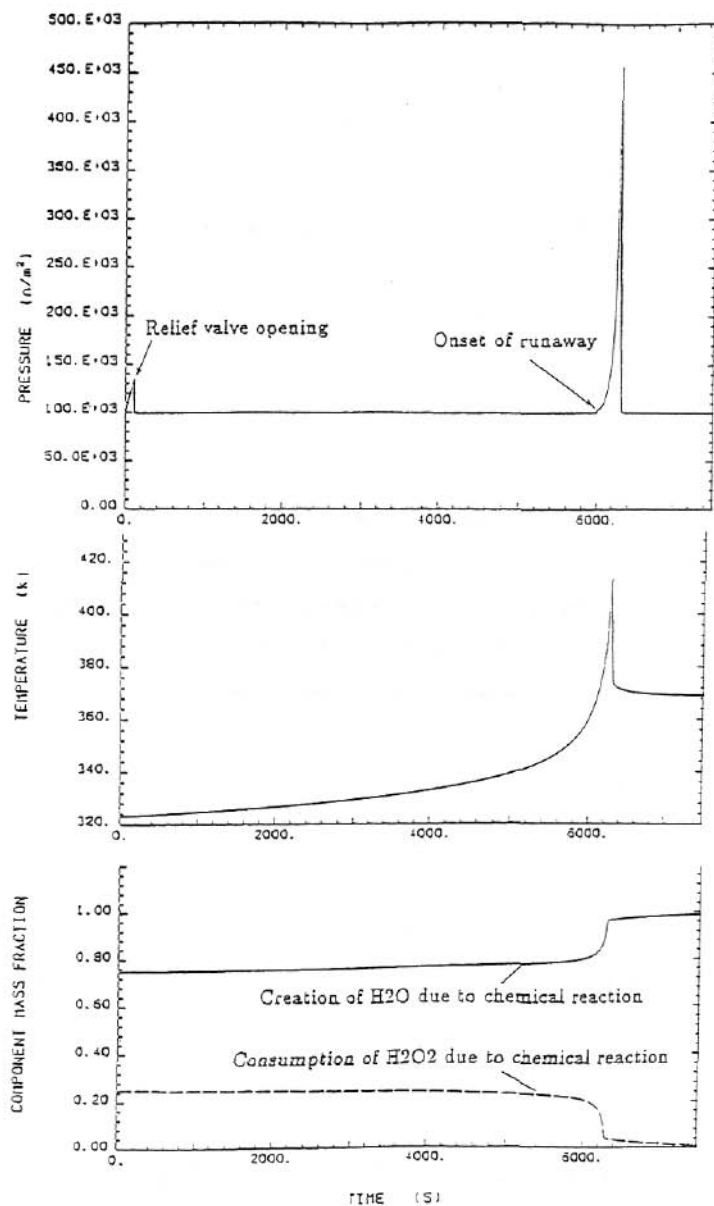


Fig 3. Pressure, temperature and mass fraction histories
(vent dia 7.8cm)

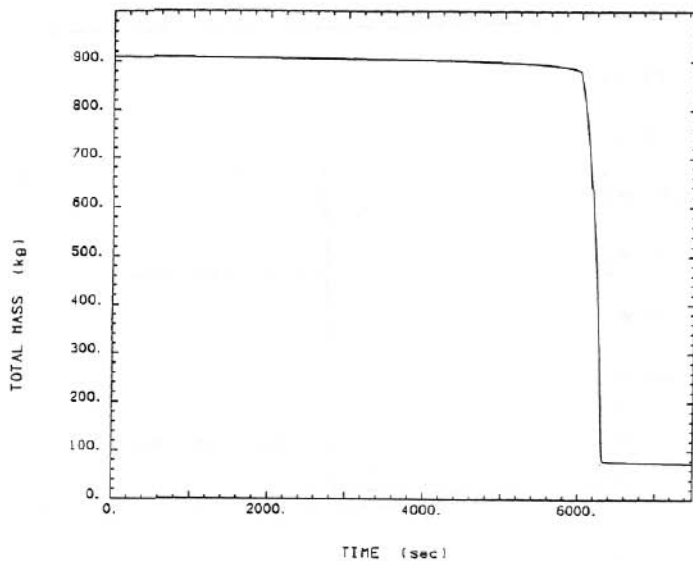


Fig 4. Mass inventory history (vent dia 7.8cm)

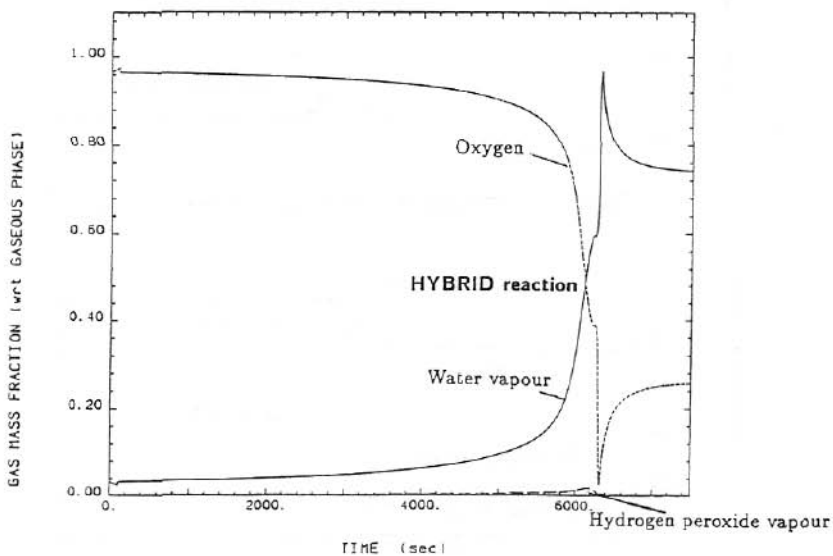


Fig 5. Relative gas mass fraction history (vent diam 7.8cm)

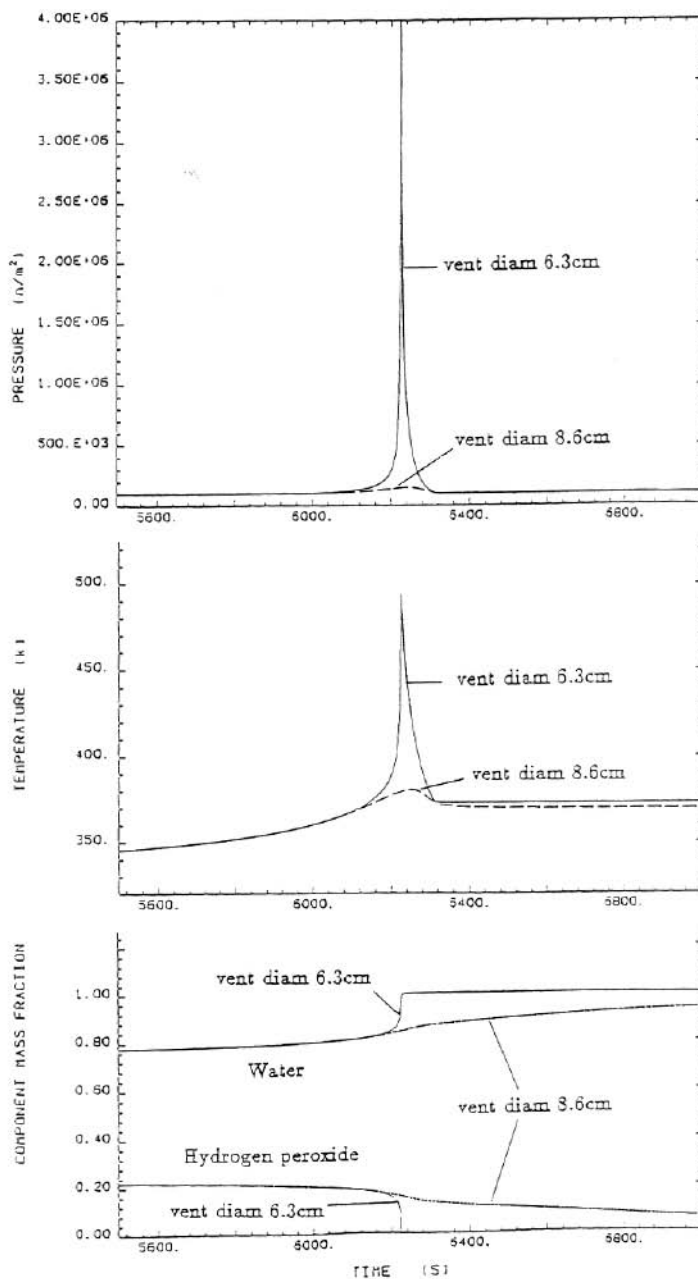


Fig 6. Pressure, temperature and mass fraction histories

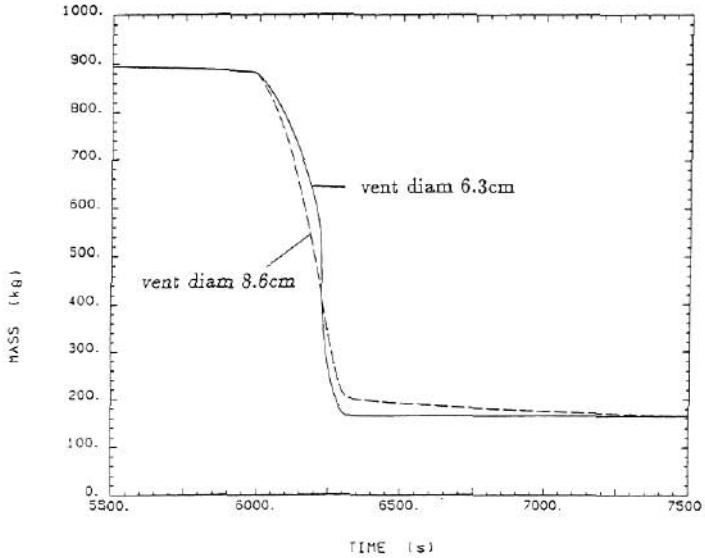


Fig 7. Mass inventory histories

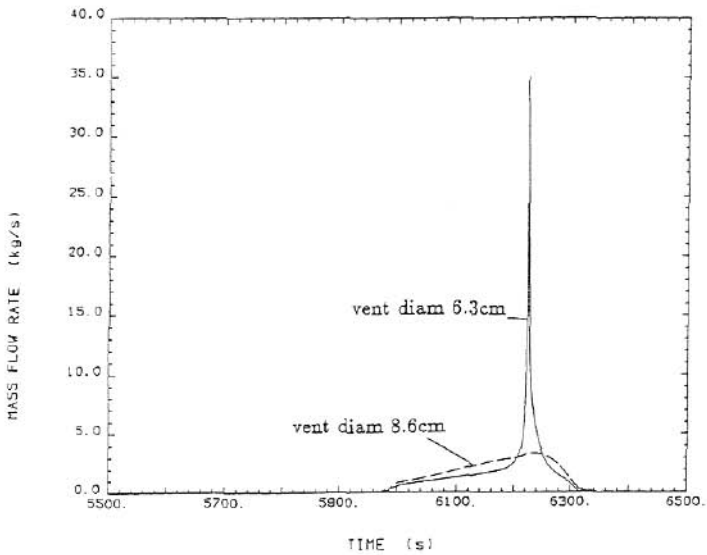


Fig 8. Vent mass flow histories

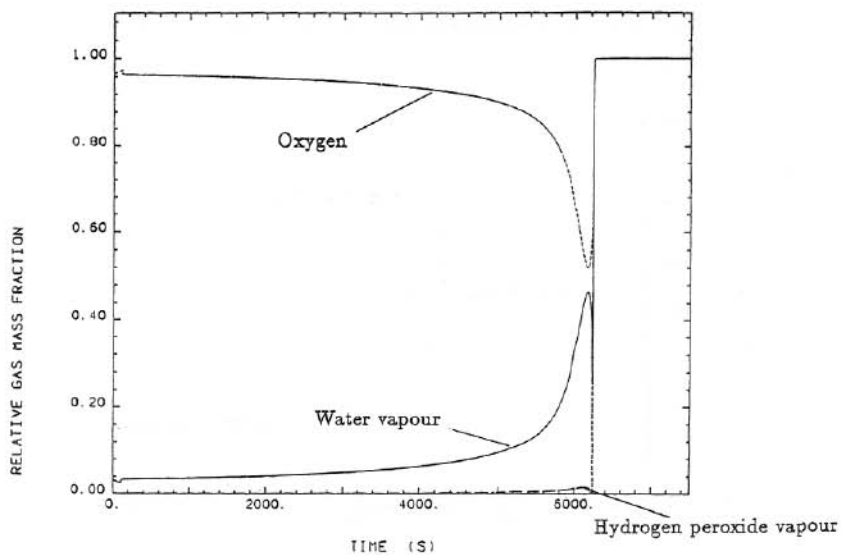


Fig 9. Relative gas mass fraction history (vent diam 6.3cm)

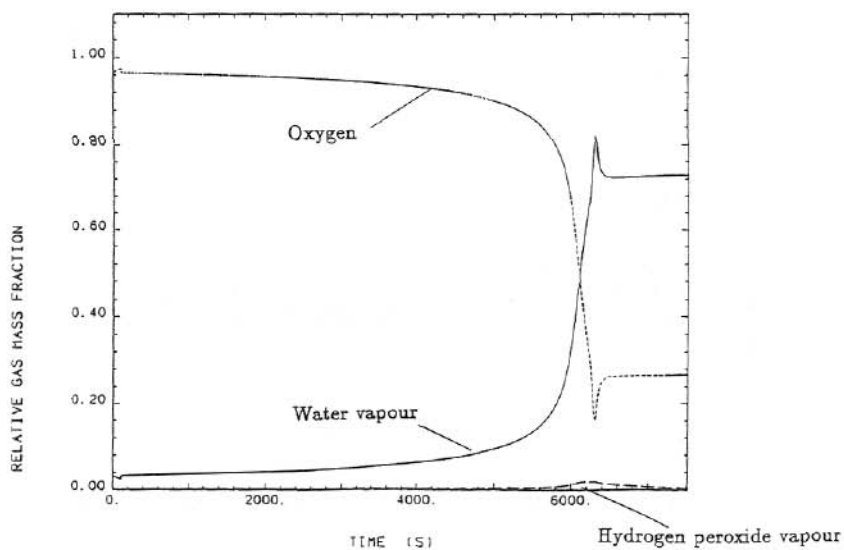


Fig 10. Relative gas mass fraction history (vent diam 8.6cm)

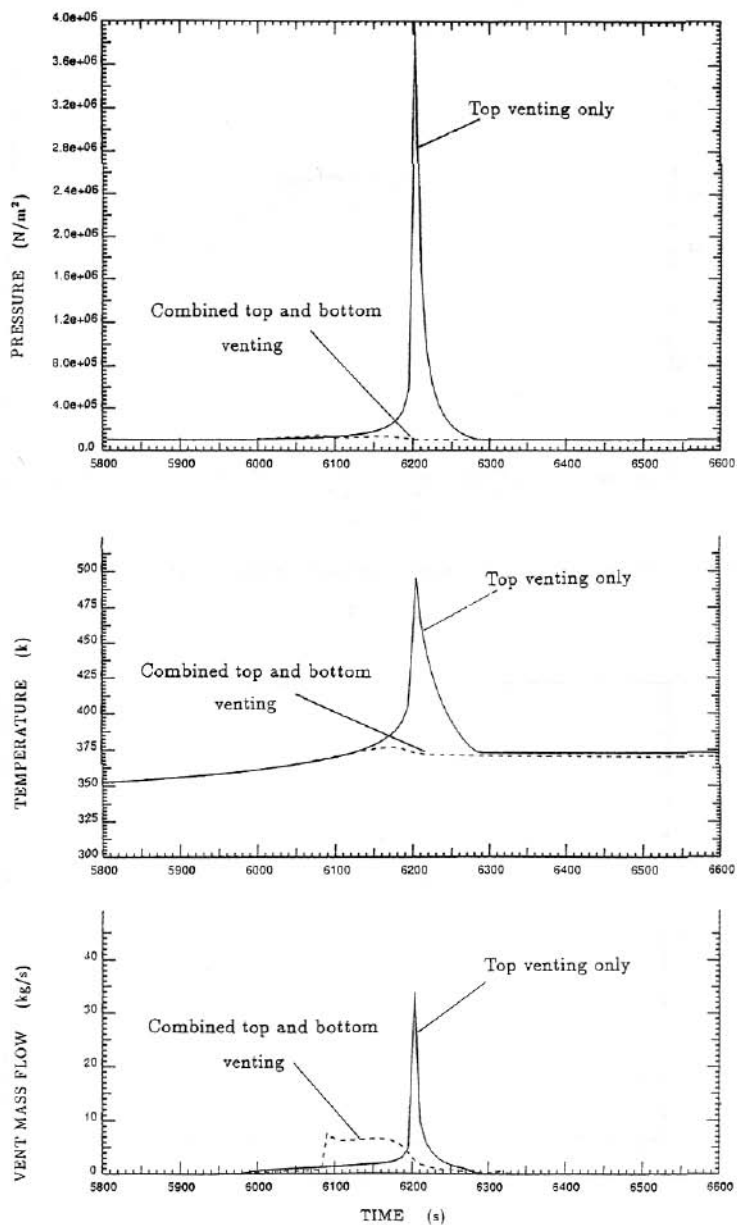


Fig 11. Pressure, temperature and vent mass flow histories

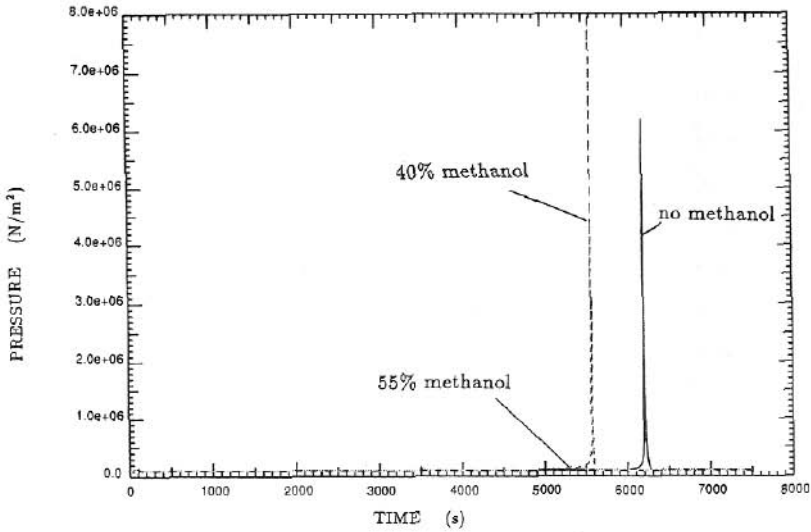


Fig 12. Pressure histories with different water/methanol concentrations

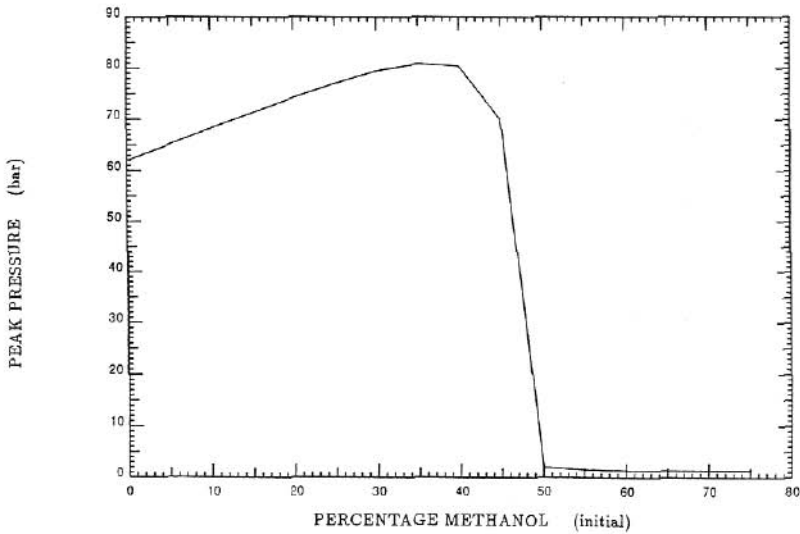


Fig 13. Locus of peak pressure for different initial methanol concentrations

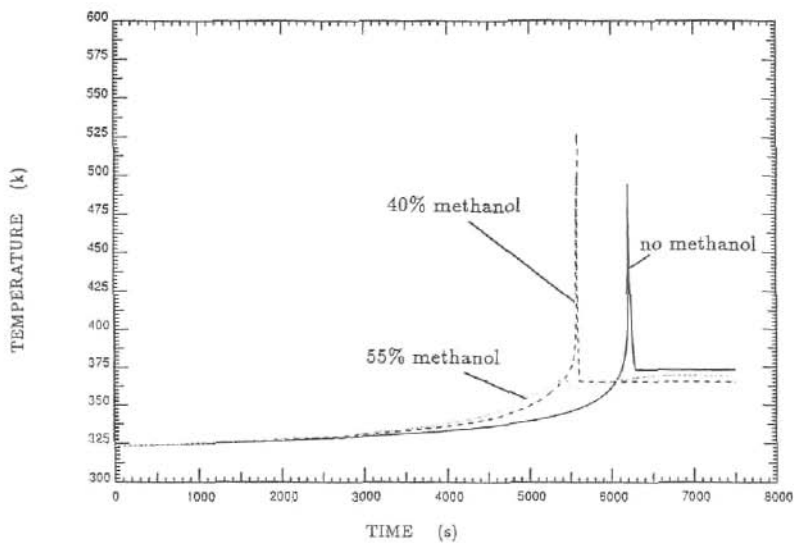


Fig 14. Temperature histories with different water/methanol concentrations