RELIEF SYSTEM DESIGN FOR EXOTHERMIC RUNAWAY: THE HSE STRATEGY

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Of the measures used to protect reactors, emergency relief systems are probably the most commonly used in the UK. Although much work has been done on relief system sizing, particularly in the US by the Design Institute for Emergency Relief Systems (DIERS), a recent HSE survey found that there is still a need for more information, particularly by design engineers in small/ medium sized companies. In response to the need for more guidance, HSE has recently prepared a Workbook which concentrates on hand calculation methods for chemical reactor relief system sizing. This paper describes the current guidance by HSE and further guidance in preparation. A current campaign by HSE inspectors to assess standards in chemical reactors is also discussed.

In support of this work, HSE is also carrying out a programme of research to assist in validating the DIERS methodology, particularly the hand calculation methods. This includes a number of pilot-scale runaway reaction experiments. The experiments have also been used as an input to a European Community project on disposal system design. The tests and main conclusions of the work to date are also described. Planned work for the future will be discussed briefly.

Keywords: Chemical reactors, relief system sizing, emergency relief, exothermic runaway

INTRODUCTION

Of the range of measures that can be used to prevent or control exothermic runaway, emergency relief systems continue to be used by most companies in the UK. However, the design of such systems is complex, requiring a knowledge of process hazard assessment, chemical reaction kinetics and fluid flow.

The need for more information on emergency relief system sizing was identified over 20 years ago. Since then, a considerable amount of research has been carried out on the subject, particularly in the US by the Design Institute for Emergency Relief Systems (DIERS). This was a consortium of companies and other organisations (including HSE) that funded research between 1978 and 1985. The work has continued on a voluntary basis by both US and European DIERS Users Groups which meet regularly. Many papers have been published on reactor relief system design, and there is a DIERS Project Manual[1]. However, a recent survey by HSE[2] found that there is still a need for more information on the design methods, particularly by design engineers in small/ medium sized companies. In many cases, companies did not know the method which had been used to size the emergency relief system or had used invalid techniques.

In response to the need for more guidance, HSE has recently prepared a Workbook[3] which concentrates on DIERS hand calculation methods for chemical reactor relief system sizing. ("Hand calculation methods" are those amenable to evaluation using a pocket calculator or spreadsheet). This paper describes the current guidance by HSE and further guidance in the pipeline. In support of this work, HSE is sponsoring a programme of research to assist in validating the hand calculation methods and fill in some gaps in the technology. This includes a number of pilot-scale runaway reaction experiments. Work is also underway, in liaison with the DIERS User Groups, to test the main computer models available for relief system sizing against some of the experimental results. The main results of the work to date and work planned for the future are summarised.

Following on from the earlier survey, inspectors in HSE's Chemicals and Hazardous Installations Division (CHID) are carrying out a further series of visits to assess standards of prevention and control. The current inspection campaign is also discussed.

WORKBOOK FOR CHEMICAL REACTOR RELIEF SYSTEM SIZING

PURPOSE

The purpose of the Workbook is to give information on methods available for the sizing of emergency relief systems for exothermic runaway reactions in liquid-phase chemical reactors. It summarises the main hand calculation methods available as a result of the DIERS project and their limits of applicability. A number of worked examples are given to help the reader apply them. The experimental information required to size an emergency relief system properly is also discussed.

The Workbook is written mainly for chemical engineers or applied chemists with a good basic training in both chemical reaction kinetics and fluid flow. It is particularly aimed at engineers in small to medium sized companies who may not have had ready access to the DIERS meetings. However, experience in the development of appropriate physical properties from databases (or small-scale experiments) for the reacting mixtures under consideration will be needed. In addition, such companies will need to obtain advice on the application of small scale calorimetry, if they do not have their own "in-house" expertise.

The Workbook should also be useful to others who, whilst they may not wish to design a relief system themselves, want to ensure that the correct procedures have been followed during relief system design for their processes.

SCOPE

The Workbook is intended to be self-sufficient for sizing calculations for the more straightforward applications. The emphasis is on the use of equations that can be solved with a pocket calculator, rather than on more complex computer models.

Unlike relief system sizing for non reacting systems, a considerable amount of experimental information is normally required for the design of chemical reactor relief systems. It is necessary to assess all the credible maloperations and system failures that may occur on the process/plant to determine the reaction runaway that requires the largest relief system. The Workbook summarises the main steps necessary to do this. Reaction hazard assessment, other than for the purposes of relief system sizing, is not dealt with. Information on this is given in reference 4.

Although there have been considerable advances in the technology over the last 20 years, it is still evolving. The information contained in the Workbook is a summary of the best available technology. Much work is still to be done and the design of relief systems for certain types of systems, e.g. viscous systems and systems containing significant levels of solids, is still complex and is outside the scope of the document. Where emergency relief system design for any particular system is outside the scope of the Workbook, the reader is referred elsewhere, e.g. to specialist computer models.

The Workbook does not deal with fire relief of vessels (except where external fire modifies the relief sizing for runaway exothermic reaction) or with the mechanical integrity of either the process vessels or relief systems. Guidance on these is available elsewhere[5]. It also does not deal with explosion venting (when the reaction proceeds as a front or wave through the liquid).

APPROACH TAKEN

The Workbook is concerned with "how to?" more than with "why?". Sizing methods are given together with conditions of applicability and some limited background information. Sources of information for theory, derivations of equations and some more unusual methods are referenced. Use is made of decision trees to guide the user to the appropriate part(s) of the Workbook. Worked examples are given for all the recommended methods.

A contents list for the Workbook is given in Table 1 and the structure is summarised by the flowchart in Figure 1 which indicates the paths to be taken through the Workbook when carrying out any particular relief system design.

Table 1: Contents of the Workbook

Chapters	Annexes
Foreword	
1. Introduction	A1 Basis of safety
2. Overview	A2 Experimental methods
3. Determining the worst case	A3 Level swell calculations
4. Classification of relief systems	A4 Computer codes
5. Relief system sizing	A5 Additional sizing methods
6. Vapour pressure systems	A6 Sizing for single phase relief
7. Gassy systems	A7 Safety factors
8. Hybrid Systems	A8 The Omega method
9. Calculation of two-phase flow capacity	A9 Glossary
10. Special cases	A10 Nomenclature
11. Disposal systems	A11 Index
12. Reaction forces	
13. Maintenance of hardware and software	

The first two chapters of the Workbook contain background information. In the Introduction (Chapter 1), it is emphasised that there are a number of means of achieving safe operation of chemical reactors. The best option being to avoid the hazards completely, or at least minimise them, by inherently safer design. However, in many cases this is not practicable and, to maintain a viable process, other safety measures will be needed, either alone or in combination. Information on the various options and the main advantages and disadvantages of emergency relief systems are discussed in Annex 1 of the Workbook.

The Introduction also lists the information required for the design of emergency relief systems for exothermic runaway. This includes:

a) The credible maloperations and system failures that might occur during reaction.

b) The kinetics of the reaction under runaway conditions.

c) Whether the reaction pressure is from vapour or gas (or both), as these require different design concepts.

d) The flow regimes, both in the vessel and relief system, during relief.

e) The design and layout of the relief system.

Unless such information is obtained and applied properly in its design, then an emergency relief system may be wrongly sized and a false sense of security placed upon it.

Chapter 2 gives an overview of the Workbook from the point of view of its use during the design process of a pressure relief system for a chemical reactor. Figure 2 illustrates the steps in the design of a pressure relief system, and indicates those steps which are covered by the Workbook.

The design process begins with Chapter 3 which explains the process of determining the worst case relief scenario on which the relief system design is to be based. This process entails determining the credible combination of failures and maloperations which gives rise to the largest required relief size. The next stage in the design process, described in Chapter 4, is to determine the system type for the purposes of relief sizing: vapour pressure, gassy or hybrid (a mixture of gassy and vapour pressure). The determination of system type is very important as this will affect the design method selected. Small-scale experiments are involved, which are described in Annex 2. Chapter 4 also deals with the determination of whether the relief flow will be:

(i) two-phase or gas/vapour only; and
(ii) laminar rather than turbulent.

These factors will also affect the design method selected.

Chapter 5 gives important background information about relief sizing, including a decision tree for selecting the chapter or annex to be used for sizing in a particular case. The relief sizing itself can then be carried out.

Chapters 6, 7 and 8 give methods for calculating the relief system size for each system type. In most cases, the simplest and most usual methods are given first, followed by references to valid alternative methods (which are given in the Annexes) should the initial methods be inapplicable or likely to oversize due to their underlying assumptions.

Chapter 9 contains important background information about two-phase flow, and calculation methods for the two-phase mass flow capacity per unit area, G, which is required to obtain the relief area for most of the relief sizing methods. Some system types are special cases involving laminar flow, solids and/or multiple liquid phases. In these cases Chapter 10, rather than Chapter 9, should be used for this calculation.

Chapters 11 - 13 cover the selection and sizing of downstream disposal systems, reaction forces which require piping and vessel supports, maintenance, documentation and change management. Useful material by CCPS on disposal system selection and sizing[6] is recommended. Additional material is given in Annexes 1 to 8 and is referenced from the text as required. This includes consideration of the safety factor to be applied to the calculated relief size.

The design of a relief system often involves iteration and recycle. The Flowchart in Figure 1 shows that possible recycle in the design process may involve changing the assumptions about the worst case relief scenario or changing the sizing method used.

FURTHER GUIDANCE

It is recognised that, despite all attempts to make the Workbook as user friendly as possible, the Workbook is still complex. It contains a number of concepts not taught at most British Universities. Consequently, a number of companies have requested further training and HSE is hoping to part sponsor a short training course, which will be aimed at giving attendees an opportunity to ask questions and carry out worked examples, with the help of experts in the Field.

Those wishing to get more expertise may wish to attend meetings of the US DIERS Users Group, which also enables practitioners to discuss technical problems with experts in the Field. US DIERS also runs training courses, set at a fairly high level. Those with more expertise may wish to join the European Users Group, however membership is relatively restricted.

More general guidance on relief system sizing, putting it into context with the other safety measures available for the prevention and control of exothermic runaway, is given in a recent HSE Guidance Booklet[7].

HSE RESEARCH STRATEGY

INTRODUCTION

To further validate the DIERS hand calculation methods, HSE's Technology Division has instigated a programme of research. Most of this is being carried out by the HSE's Health and Safety Laboratory (HSL) at Buxton where a 350 litre pilot-scale chemical reactor plant has been built specifically to carry out vented runaway chemical reactions[8]. Small scale calorimeters are used to predict the overpressures in the large scale test, using the main hand calculation methods, and these are then compared with the experimental overpressures. A schematic diagram of the pilot plant is shown in Figure 3.

The pilot plant has already been used on the following systems:

(i) The esterification reaction between propionic anhydride and isobutanol, both with and without sulphuric acid catalyst. Nine experiments with various catalyst concentrations and four uncatalysed experiments were performed using different vent diameters, relief set pressures and jacket temperatures.

(ii) The esterification reaction between propionic anhydride and isopropanol, catalysed by sulphuric acid. Seven experiments were performed. The reaction rate was varied by using various catalyst concentrations. A number of different vent diameters were used in the tests. The jacket temperature was held at 75^{o}C, and the relief set pressure at 1.5 bara.

(iii) The decomposition of *tert*-butyl peroxy-2-ethylhexanoate (a peroxy-ester) in a high boiling point solvent, catalysed by cobalt octoate. Eight experiments were performed with various concentrations of catalyst and different vent diameters but with the same jacket temperature (95^{o}C) and relief set pressure (2.0 bara).

Systems (i) and (ii) are examples of vapour generating systems and system (iii) is a gas generating system.

Further work is underway on the hydrolysis of acetic anhydride, with and without surfactant. The presence of surfactant allows the effect of foamy behaviour, which is present in many industrial systems, to be investigated. This is thought to result in higher pressures than non-foamy systems.

Most of the tests were used without any quench fluid in the containment tank. However, four separate tests were performed using a conventional quench system as part of a joint EC project entitled ***C**hemical **H**azard **E**valuation and **E**mergency **R**elief **S**ystems* (CHEERS)[9]. Two types of reaction system (one vapour pressure and one gassy) were investigated.

EXPERIMENTAL RESULTS

The following parameters are measured:

(i) Temperature and pressure in the reactor, relief line and containment system and these are plotted against time.

(ii) Mass discharge rate from the reactor. (This can be deduced from the response of load cells mounted below the catch tank and on the vent line.)

(iii) Void fraction in the vent line using a gamma ray densitometer.

Video cameras are used to monitor level swell in the reactor, and flow along the relief line and into the containment tank.

Figure 4 shows the reactor temperature and pressure records from one of the system (ii) (vapour pressure) pilot-scale experiments. Two-phase flow occurred immediately after vent opening when the temperature in the vapour space became approximately equal to the liquid temperature measured at the bottom of the vessel. The temperature continued to rise after vent opening and an overpressure of approximately 50 % of the relief-set pressure was reached.

Figure 5 shows the reactor temperature and pressure records from one of the system (iii) (gassy) pilot-scale tests. In contrast to the vapour system results, the reactor pressure returns to atmospheric soon after vent opening. However, the operation of the relief system does not affect the rate of temperature rise in the vessel. The reaction rate continues to rise until the rate of gas evolution is sufficient to cause two-phase flow. The onset of two-phase flow is indicated by an increase in reactor pressure and a corresponding sharp increase in the temperature at the top of the vessel.

CONCLUSIONS OF EXPERIMENTAL WORK

The work has shown the following main results/ conclusions:

(a) For systems (i) and (ii) (vapour pressure), the hand calculation methods[3] were always conservative when used within their limits of applicability. Both single phase vapour venting and two-phase liquid and vapour venting occurred. When two-phase venting did occur, densitometer measurements indicated high vapour fractions in the discharge from the reactor. This effect is to be investigated further.

(b) For system (iii) (gassy), the experimental overpressures were initially found to substantially exceed the calculated values. This difference is attributable to the effect of dissolved gas in the calorimetric tests, leading to an underestimation of the gas generation rate. Once corrections were made for this effect, calculated values[3] lie well above the experimental values, indicating that safe vent sizes can be obtained by this procedure. The effect of dissolved gas can be overcome by modifying the test procedure[3]. Further work is being undertaken to investigate the effects of dissolved gas.

(c) Further work is needed to accurately predict the degree of reactant level swell during venting (used in some of the less common hand calculation methods). This will also affect disposal system design and HSE is planning a collaborative project in this area, which will also investigate the effects of “foaminess” on venting.

(d) The quench tests indicated that the use of a sparger and quench system causes a substantial reduction in the amount of liquid or condensable vapour vented to atmosphere for both vapour pressure and gassy systems. Under the conditions of the pilot-scale experiments, the sparger reduced the mass of liquid or condensable vapour vented to atmosphere to a level which would be hazardous only for very toxic decomposition products. The detailed results of this investigation have been submitted to the European Commission[9]. HSE are planning to do further work in this area.

ROUND ROBIN

Details of one of the series (ii) experiments were distributed to volunteers via the US and European DIERS Users Groups and the volunteers were invited to predict the maximum pressure (and other parameters) without access to the experimental results. Participants have used a variety of sizing methods, including hand-calculations and commercial computer codes. A comparison of predictions and experimental results is to be fed back to the participants at forthcoming DIERS Users Group meetings to promote discussion and improvements to computer models. It would be premature to release results in this paper. However, the exercise has highlighted the importance of using the correct input data in vent sizing calculations, whether by hand or using computers.

FUTURE WORK

Once HSE have had the opportunity to evaluate these series of experiments, they will be published as an HSE Contract Research Report. This will allow wider dissemination of the results and discussion with the industry. Some more detailed information is already available in a published paper[10]. HSE are also participating in an EC project aimed at producing more information on venting of viscous systems. Further projects on assessing the reaction forces generated during relief and venting of systems containing solids are also planned. Ultimately as the technology develops further, it will be necessary to update the existing guidance, both on relief and disposal system design.

HSE INSPECTION CAMPAIGN

The results of the survey on relief system sizing were presented to members of the Health and Safety Commission's Advisory Committee on Dangerous Substances, a tripartite body comprising representatives from the industry, the Unions and the Local Authorities. This raised considerable concern to the Committee members and, as a result, HSE has undertaken to complete a number of actions. In particular, inspectors in HSE's Chemicals and Hazardous Installations Division (CHID) have been undertaking a series of visits to further assess standards of assessment and control of exothermic reaction hazards. A structured proforma has been prepared for use by inspectors during the visits and the responses are being collated centrally.

This project, which is now in its final year, is proceeding satisfactorily. The most common subject of advice to occupiers being given by inspectors addresses a lack of evidence, particularly documentation, to demonstrate that exothermic reactions have been adequately assessed and understood, which is fundamental to the selection of an appropriate basis of safety including relief system design. At the conclusion of the project a report will be prepared for the Chemicals Industry Forum, which provides a meeting ground between HSE and industry. The results of the project will be used to assist HSE in its guidance and inspection strategy for the future.

CONCLUSIONS

1. The design of emergency relief systems for chemical reactors is an extremely complex area, which is only understood by a relatively small number of experts.

2. In order to provide further guidance HSE have written a Workbook which summarises the best available technology.

3. In the initial series of pilot-scale runaway reaction experiments, the hand calculation methods for relief system sizing were conservative. Further work is underway on foamy systems, which is likely to be a more severe test.

4. HSE, in liaison with others, is carrying out further research, but this work may take several years to complete. Input from the industry is welcomed and a collaborative proposal on disposal system design has been put forward.

5. In view of the difficulties in designing adequate emergency relief systems for chemical reactors, the need to avoid the hazard of runaway, preferably by inherently safer design methods, or, where this is not viable, by closer control of the reaction system is emphasised. Alternatively companies may wish to consider other protective measures such as reaction inhibition.

6. The results of the Round Robin exercise, to compare the predictions of computer models with experimental results, has highlighted the importance of using the correct input data in vent sizing calculations.

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The views expressed in this paper are those of the authors and not necessarily those of the Health and Safety Executive.

FIGURE 1 Flowchart for the use of the Workbook

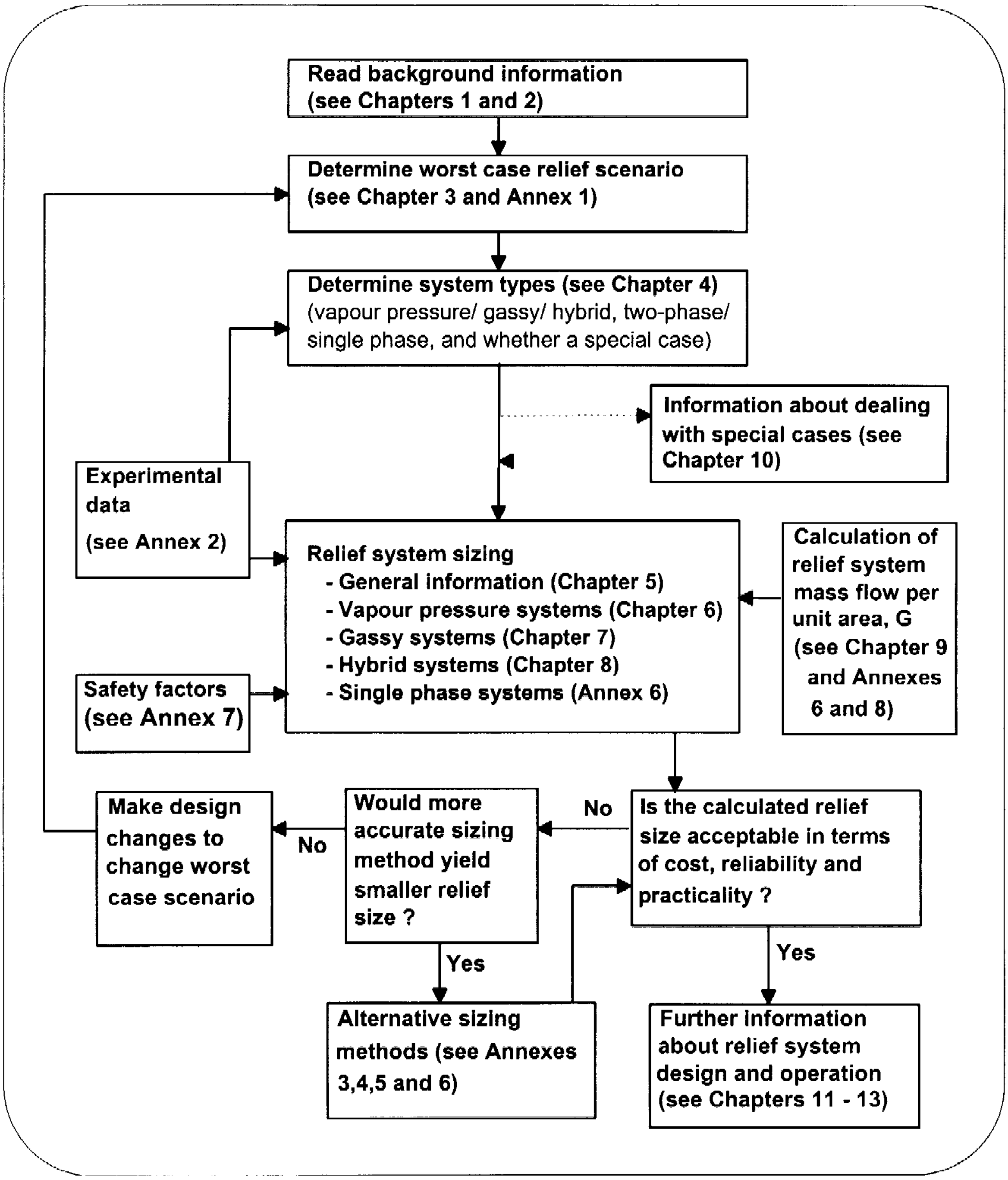

FIGURE 2 Steps in the design of a relief systems for a runaway chemical reaction

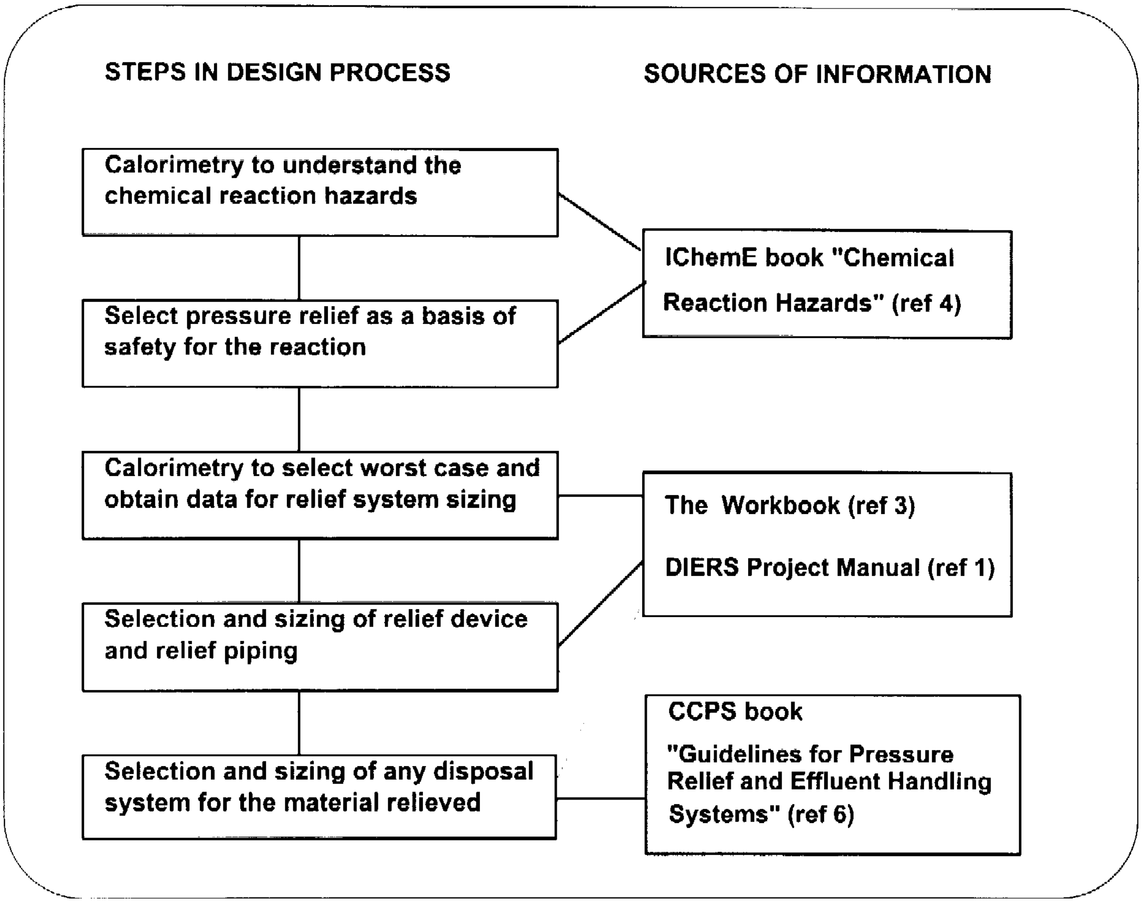

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FIGURE 3 Schematic diagram of pilot plant reactor

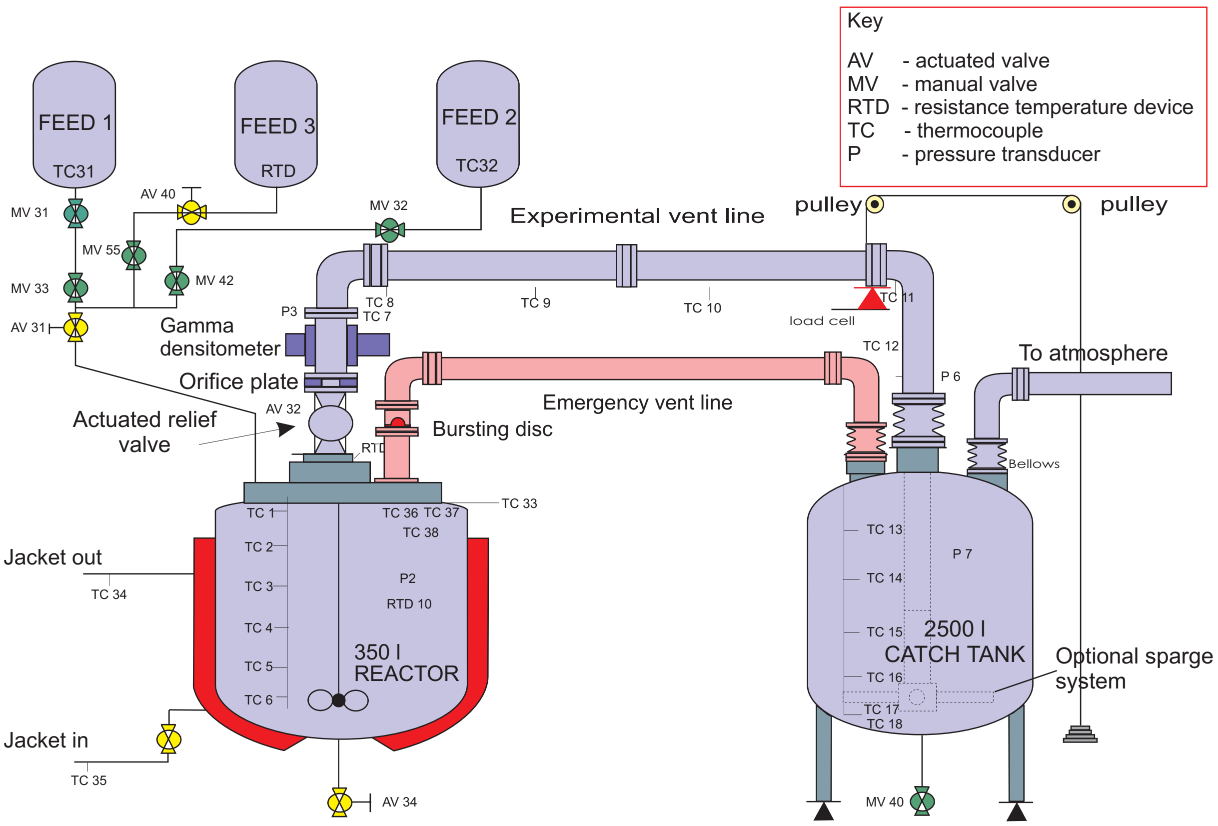

FIGURE 4 ..Reactor temperature and pressure records for a vapour pressure system

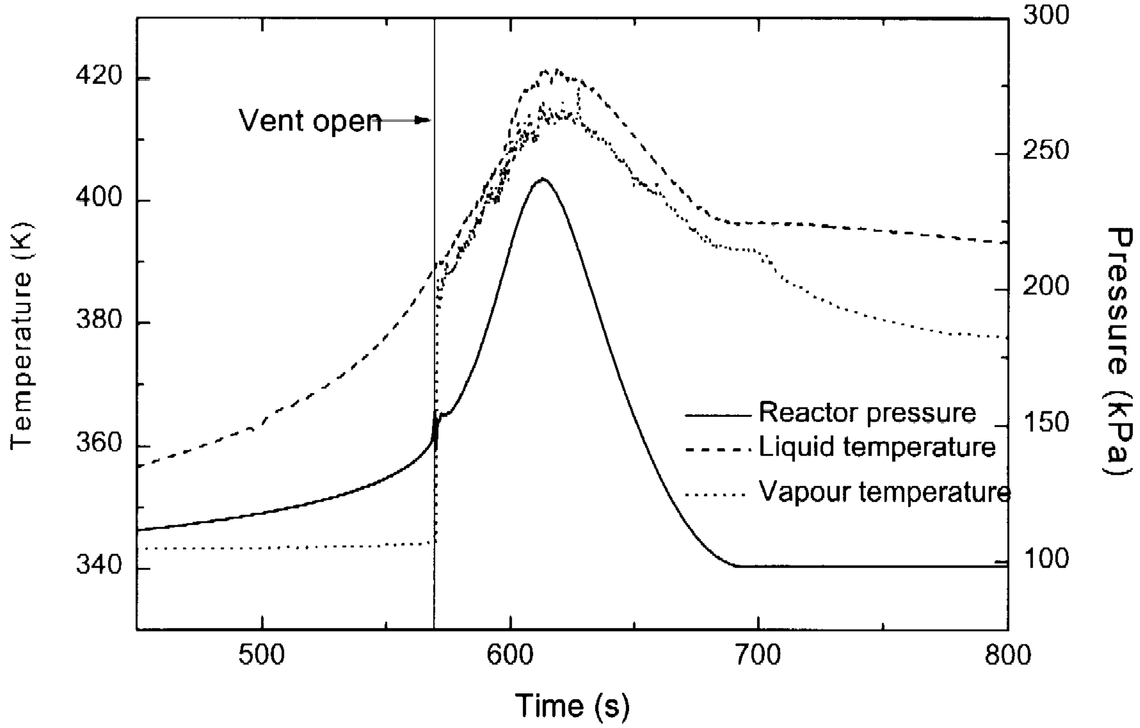

FIGURE 5 Reactor temperature and pressure records for a gassy systems