CALCULATION METHODS FOR REACTOR RELIEF : A PERSPECTIVE BASED ON ICI EXPERIENCE

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ICI experience of calculation methods for reactor relief system sizing is reviewed, with the emphasis on the improvements in design efficiency yielded by appropriate use of DIERS techniques when applicable. The continuing validity of some former methods will be be discussed.

Reactor, Relief, DIERS, Two-phase.

1. INTRODUCTION

Calculation methods for sizing relief systems for reactors were reviewed in 1980 by Duxbury (1), and the methods recommended in that paper continue to be valid. The advice on heat loss/adiabaticity of test vessels is amplified below. DIERS, the Design Institute for Emergency Relief Systems, was formed in 1978 under the auspices of the A.I.Ch.E., and its 29 member companies, including ICI, funded research costing $1.6 million into reactor relief sizing methods. This work was completed in 1985, and a number of new calculation methods have been proposed.

At ICI, we have used the new methods selectively as they became available and have now used the new methods in over 40 applications and have assessed their applicability to some 30 others. This compares with some hundreds of vent sizings done pre DIERS, and the experience gained of the DIERS methods will be discussed in this context. It is not the purpose of this paper to discuss either the choice of worst case design conditions or the experimental techniques for providing kinetic data. However, it should be emphasised that the choice of worst case design conditions is a crucial step in the vent sizing procedure and needs great care. Also, design data (usually) and scale-up data (always) have to be obtained in highly adiabatic test reactors, where heat loss from the contents to the wall is negligible. It is not sufficient to eliminate losses from the vessel to atmosphere.

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2. CALCULATION METHODS FOR VENT SIZING

2.1 GENERAL

Table 1 lists those vent sizing methods which will be discussed in this paper. Methods A-F were all in use before DIERS, and are discussed in detail in (1). They continue to be valid where applicable (but see previous paragraph with reference to adiabaticity of test vessels). DIERS has made further contributions to some of these methods eg scale-up and computer programs. Methods G-J are new methods proposed by DIERS.

The former FIA (Factory Insurance Association) Method (19) is not discussed. Other methods are preferable because of its illogical basis (heat release per unit volume, not rate of heat release), and lack of any dependence on fluid properties, pressure, phase-nature of flow, line length, and fill ratio (1). Industrial Risk Insurers (IRI), the successors to FIA, have withdrawn it from their Engineering Procedures.

Method A, vapour or gas-only venting is included for completeness but has limited applicability to reactor vent sizing. Two phase flow can usually be expected to occur from a runaway reactor vent and the assumption of two phase flow must usually be made as a safe case (but see section 3 below). All the methods apart from A either assume two-phase flow or allow the assumption of two-phase flow to be made.

It is usually preferable to set the relief device on a reactor to operate at a pressure well below the design pressure. This allows the vent to open at a low pressure, and hence usually at a low temperature, when the runaway reaction is still at a relatively low rate. Also, the pressure may now be permitted to rise during venting. Thus, if two-phase relief occurs, the vent can be sized such that the reactor empties sufficiently for the pressure to pass through a maximum and then fall, before the maximum vessel pressure allowable has been exceeded.

In this paper, as in many of the references quoted, the term "set-pressure" will be used to denote the pressure at which the relief device is known to be fully open. For a safety valve this will often be at 10% above the actual set pressure, since a 10% higher pressure is often needed to fully open the valve. For a bursting disc device, the (redefined) "set-pressure" will correspond to the nominal bursting pressure plus tolerances or to the maximum specified bursting pressure of the device. The term "overpressure" will be used to mean the difference between the (redefined) set-pressure and the maximum pressure attained during the vented runaway reaction. Please note that these definitions are not the same as those used in British Standards.

In order to help decide which methods are applicable in a given case, it is first necessary to redefine the chemical system as one of the following types:-

a) "Vapour pressure systems", in which the pressure generated by the runaway 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 a permanent gas which is generated by the reaction. DIERS has not produced any new vent sizing calculation methods for gassy systems.

c) "Hybrid systems", in which the total pressure is due to both vapour pressure and permanent gas generation. In some hybrid systems, the vapour generation in a vented reaction is high enough to remove sufficient latent heat to "temper" the run-away i.e. to hold the temperature constant. So far, the authors have no experience of vent sizing for hybrid systems, and they are not discussed further in this paper.

2.2 VAPOUR PRESSURE SYSTEMS

The new DIERS methods which have been proposed for vapour pressure systems are G-J in Table 1. (Two new computer programs, SAFIRE and DEERS, were also produced for DIERS and are discussed further in 2.4 below.) These new methods, in common with previous methods, assume that vapour/liquid equilibrium is maintained in the vessel during relief.

Fauske's short-form equation and nomogram (methods G & H)

Method G, Fauske's short-form equation, is a simple formula based on the modified Boyle method (Method C) and incorporating a simplified version of the equilibrium rate model (ref 13) for two phase vent flow. This method has advantages over the modified Boyle method in that it tends to be quicker and less conservative. The essential parameter of that method, the Boyle time, is not needed explicitly.

The method is limited to overpressure in the range 10-30% of set pressure and to short vent line lengths; it also assumes that the flow is turbulent and that the vapour behaves as an ideal gas.

Method H is a nomogram based on method G for the specific case of 20% absolute overpressure, and assumptions as to typical values of physical properties have been made in its construction. The authors would only use this method to get a preliminary order-of-magnitude feel for the vent size required.

Leung's Method (Method J)

Method J (Leung's long-form equation), given here,

$$A = \frac{\frac{m_o}{q}}{G\left[\left(\frac{VT}{m_o}\frac{dP}{dT}\right)^{0.5} + (C\ \Delta T)^{0.5}\right]^2}$$

is an analytical solution to the differential heat and mass balance equations during venting. This makes it potentially more accurate and less conservative than methods G and H. There are also fewer limitations on its applicability, in that it is stated in Ref 16 to be valid from 0-50% overpressure, and also the vent flow capacity per unit area (G) is included explicity in the formula. This allows any appropriate vent capacity calculation method to be used, so that the method can be used even for a long vent pipe.

In ICI, we use Leung's method (J) as our preferred vent sizing method for vapour pressure systems. Even in cases when method G is also valid, method J is preferred since the only additional data needed is dP/dT, which is usually known, and method J takes little additional time to evaluate compared with G.

The Authors also prefer Leung's method (J) to Huff's pseudo-steady-state method (method F). Huff's method gives similar accuracy to Leung's method in most cases. For example, the comparison given in Table 1 of reference 11 shows a difference of less than 3% between the diameters calculated by the two methods. However, Huff's method takes longer to evaluate since it requires the simultaneous solution of three equations, usually by trial and error. The quicker, but more approximate version of Huff's method tends to be more accurate than the "short-form" equation (method G) but, again, takes longer to evaluate.

A maximum overpressure of 50% has been recommended when using method J (16). The formula tends to become increasingly conservative at high overpressures for the following reasons:

a) the arithmetic mean heat evolution rate per unit mass of reactants, between the set pressure and the maximum pressure, is used. The heat evolution rate rises exponentially with pressure, so the arithmetic mean over-estimates the true average, particularly for high overpressure.

b) the vent capacity per unit area at the set pressure is used.

The result of the above is that, in many cases, the calculated vent area (see figure 1) decreases with increasing overpressure (as expected) but then reaches a minimum value and thereafter increases with increasing overpressure. The minimum area usually, but not always, corresponds to overpressures above 50%. It is recommended that, for high allowable overpressures, the vent size is evaluated at the maximum allowable overpressure and also at a slightly lower overpressure. If the lower overpressure gives a smaller vent size, the calculation should be repeated for progressively lower overpressures, and the minimum vent size obtained should be adopted.

The derivation of method J (ref 11) involves integrating the differential heat and mass balances assuming the heat evolution rate per unit mass, the vent capacity per unit area, and physical properties (latent heat, liquid specific heat and vapour/liquid specific volumes) are constant. Of these parameters, the heat

evolution rate and vapour specific volume tend to be the most sensitive to pressure. In order to decide the maximum overpressure for which the method is valid in a particular application, we would compare the values of the above parameters, at the set pressure and at the proposed maximum pressure, and make a judgement as to whether the use of average values is reasonable, or whether it would be likely to lead to gross oversizing.

When calculating the vent line capacity per unit area, the authors assume that flashing to equilibrium occurs, as recommended by DIERS (10). This is a safe assumption for vent sizing purposes, since a higher flow rate would result if equilibrium was not reached in the vent. It is also likely to be a realistic assumption since the length required to reach equilibrium is only about 0.1 metres (13) and most vents will be at least this long.

The authors use the simplified form of the equilibrium rate model (ERM) below (13) to calculate vent capacity per unit area, whenever it is applicable, because it is so quick and easy to use and requires few data (and these are usually readily available).

$$G = \frac{dP}{dT}\sqrt{\frac{T}{C}} = \frac{h_{fg}}{v_{fg}\sqrt{C\ T}}$$

The conditions of applicability for this model are:

- negligible friction ie safety valve or bursting disc with short vent pipe.
- vapour is an ideal gas; liquid is incompressible.
- turbulent flow.

In cases where the equilibrium rate model (ERM) is inapplicable (eg because of a long vent line, perhaps with sections of different diameter, or static head changes, or because of non-ideal physical properties) the authors use an in-house fluid flow computer program based on HTFS methods to calculate the vent capacity. When venting is via a safety valve, its sizing is usually done using the ERM. When pipework layouts are available, the fluid flow program is used to check that pressure drops upstream and downstream of the valve are acceptable. For bursting disc systems, a correction factor to the ERM for vent line length has been given (12). This can be useful for preliminary sizing purposes, but since it assumes a constant diameter vent pipe and no static head changes, it is of limited applicability and the final vent capacity calculation would usually be done using the fluid flow program.

The use of Leung's method (J) for vent sizing, particularly in cases where the ERM is applicable for vent capacity, has been found to be very quick, easy and efficient. In most cases, its accuracy is

sufficient for the additional accuracy of a dynamic model computer program to be neither necessary, nor warranted by the accuracy of the available data. Its use is quicker and more efficient than previously available hand-calculation methods, and it does not make gross simplifying assumptions as do Boyle (method C) and the constant pressure method (method B).

Using method J, only one calculation needs to be made for a given allowable overpressure. It was previously necessary to find the vent size for two phase venting using both methods B and C, and take the smaller (since both methods oversize for two-phase flow), and then to take the larger of this two-phase vent size and that calculated for vapour-only venting using method A. Whereas method C is known to yield vent sizes, on occasion, which are smaller than required for vapour-only relief (1) (which must be allowed for), we have yet to find an application where method J does this.

The speed of method J is such that the time taken for vent sizing is now largely limited by the time taken in determining the worst case design conditions and obtaining the design data rather than by the vent sizing calculations themselves. In rare cases, where the conditions of applicability are not satisfied, the use of a computer program may be appropriate. This is discussed in Section 2.4.

2.3 GASSY SYSTEMS

As stated previously, DIERS has produced no new approaches for this : methods B (constant pressure), D (direct vent area/vessel volume scale-up) and E (dynamic simulation computer program) remain appropriate. Two new computer programs, SAFIRE and DEERS, have been produced which may sometimes be useful. (See Section 2.4 below).

It must be remembered that design data for methods B and E (usually), and scale-up data for method D (always) has to be obtained in highly adiabatic test reactors. The heat loss from the contents to the wall and through the wall to the surroundings must be negligible : it is not sufficient to eliminate heat losses from the test vessel to atmosphere.

2.4 COMPUTER PROGRAMS : DYNAMIC MODELS OF RUNAWAY REACTOR

The use of a dynamic model to follow the course of the vented runaway reaction is potentially the most accurate vent sizing method. As part of the DIERS project two such models were written: SAFIRE (5) which was written by Fauske & Associates and made available to all DIERS members, and DEERS (6) written by JAYCOR. The authors have no experience of using the DEERS model, but have used both SAFIRE and the ICI model, IDRIS, which, unlike SAFIRE, can take account of highly non-ideal physical properties.

Dynamic models require a great deal of data, which are often not readily available. Before a model can be used, physical property data have to be collected and, if necessary, correlated in the form required by the program. Kinetic data for the runaway reaction is also needed and this must be correlated in the required way. In some cases it is necessary to write new subroutines in order to correctly model the kinetics. This means that, in using a dynamic model for reactor relief sizing, there tends to be a lead time of several days before the data have been assembled ready for vent sizing runs for a new application to be started. Also, a considerable amount of checking of the model output is usually needed before the results can be believed.

Sizing a vent using a dynamic model is an iterative process. A vent size is guessed and the model is run to find out whether this size is too big, too small or about right. The procedure is continued until the correct vent size is found. The computer run-time for each iteration can be long ($\sim$1 hour for a reasonably complex problem) so this can be expensive in computer time and man hours.

Because of their relative ease and speed of use, the authors prefer to use hand-calculation methods rather than dynamic computer models whenever possible. Also, in many cases, the quality of data available does not justify the use of a dynamic model. For example, in the styrene polymerisation example in reference 11, the SAFIRE computer program (5) would have yielded a diameter only 11% less than Leung's method (method J). By developing much-improved hand-calculation methods for vapour pressure systems, DIERS has reduced the number of cases where it is necessary to use a dynamic model and so increased the efficiency of vent sizing.

There are, however, certain but infrequent cases for which a dynamic model is an indispensable tool. These include systems for which physical properties are highly non-ideal (eg because during venting the conditions are close to the thermodynamic critical point), and cases where there is a discontinuity during the venting process (eg the reactant feed stops when the reactor pressure exceeds the feed pressure). They may also be useful for gassy systems (particularly if direct scale-up is not possible).

3. LEVEL SWELL

When a runaway reaction causes vaporisation or gas evolution, bubbles of gas/vapour are generated within the liquid. They then usually rise through the liquid and disengage at the surface. Whilst the bubbles remain within the liquid, they occupy volume and so cause the liquid level to rise or "swell". See Figure 2. If the level rises as far as the vent, two-phase venting will occur. DIERS has developed methods to predict the extent of level swell (14), and hence whether two-phase relief or vapour-only relief is to be expected, but these methods are valid only for systems which are not "natural" surface-active foamers.

Surface-active foaming systems tend to always fill the reactor with a homogeneous two-phase mixture during relief and to always vent a two-phase mixture. Only trace quantities of certain substances are needed in order to cause "natural" surface-active foaming behaviour. For this reason, DIERS (10, 14) has recommended that for reactor relief, surface-active foaming should be always assumed, resulting in a homogeneous two-phase mixture entering the vent.

In most cases the authors follow this recommendation and assume homogeneous two phase venting. However, there are certain cases where we have direct evidence that surface-active foaming behaviour does not occur. An example of such evidence would be the fact that a reflux condenser can be used to cool the reactor. If the mixture were a "natural" foamer, then the vessel would tend to fill with foam and the reflux condenser would be fed with a two-phase mixture and would not operate satisfactorily. Small-scale equipment for testing for natural surface-active foaming has been proposed (12).

If evidence is available that the mixture is not a "natural" foamer, methods in (14) can be used to calculate whether vapour-only venting will occur under runaway conditions, and, if so, the vent can be sized for vapour only. If two-phase venting is predicted initially, the level in the reactor at which two-phase venting reverts to vapour-only venting can be calculated. We would then assume homogeneous venting up to the point of disengagement, ie no credit would be taken for the fact that the two-phase mixture entering the vent before disengagement might contain a higher vapour fraction than the average for the vessel. Vent sizing can then be done using a hand-calculation method analogous to that described for vaporiser relief in (15), or by modifying either method G or method H (17).

4. CONCLUSIONS

Hand-calculation methods, developed as part of the DIERS program, have greatly improved the efficiency of reactor relief sizing in those cases for which they are applicable. It is possible to size a vent, with sufficient accuracy, in a matter of hours.

Computerised dynamic models continue to be potentially the most accurate vent sizing methods. However, in most cases, the accuracy of the data available, and the significance of any increased accuracy, do not justify the increased design time needed to use these computer models.

It is occasionally possible to demonstrate that the reacting mixture has no "natural" surface-active foaming tendency. In such cases, the relief sizing calculations can take advantage of vapour/liquid disengagement, and a smaller vent size is often possible.

The reactor relief sizing methods, recommended in reference 1, which the authors used before the DIERS methods were available, continue to be valid. (Amplification of the advice on heat loss/adiabaticity requirements for scale-up and testing has been provided). However, they tend to result in larger vent sizes i.e. are more conservative and less accurate, than the new DIERS methods. They also take longer to evaluate.

5. NOMENCLATURE

A	Vent area (m^2).
C	Liquid specific heat capacity (J/kg K).
dP/dT	Rate of change of vapour pressure with temperature = slope of vapour pressure curve at (redefined*) set pressure (N/m^2K).
h_{fg}	Latent heat of vaporisation (J/kg).
G	Vent flow capacity per unit area at the (redefined*) set pressure (kg/m^2s).
m_o	Initial mass in vessel (kg).
q	Heat evolution rate (by the exothermic reaction) per unit mass of vessel contents. The arithmetic mean value between the (redefined*) set pressure and the maximum pressure allowable should be used. (W/kg).
T	Temperature of vessel contents at (redefined*) set pressure (K).
ΔT	Temperature difference between that at the maximum pressure allowable, and that at the (redefined*) set pressure (K).
V	Vessel volume (m^3).
v_{fg}	Difference between the vapour specific volume and the liquid specific volume (m^3/kg).

6. REFERENCES

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* See Section 2.1 for definition.

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FIGURE 1

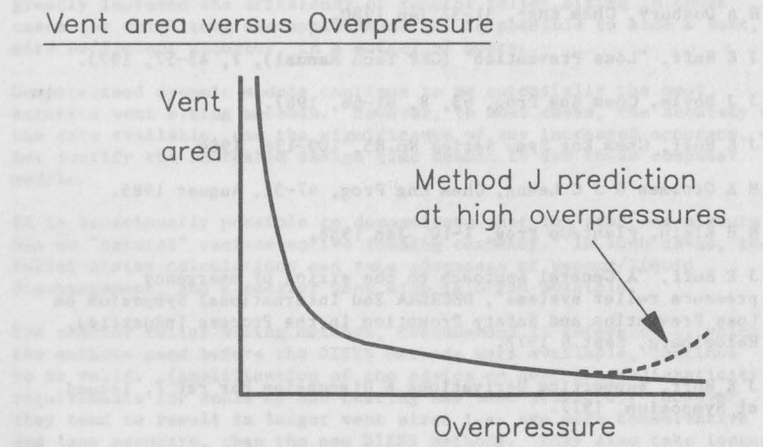

FIGURE 2

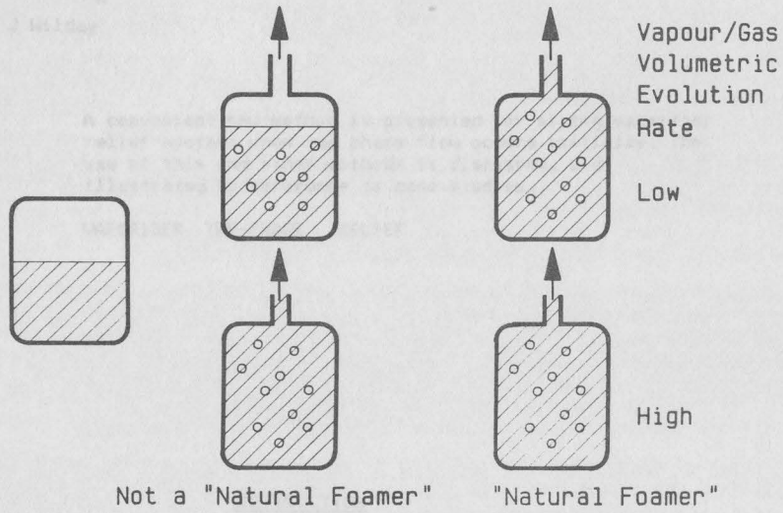

TABLE 1 LIST OF VENT SIZING CALCULATION METHODS

	DESCRIPTION	REF
A	Gas/vapour-only venting.	1
B	Two phase venting to keep pressure constant.	1, 2
C	Modified Boyle.	1, 3
D	Direct vent area/vessel volume scale-up.	1
E	Computer program - dynamic simulation	1, 4, 5, 6
F	Huff's Pseudo-steady state model.	1, 7, 8, 18
G	Fauske's (Short-form) equation.	9
H	Nomogram.	10
J	Leung's (Long-form) equation. NOTE: For comment on the former FIA sizing method, see section 2.1	11, 12