AN IMPROVED METHOD FOR SIZING BY REACTOR RELIEF SYSTEMS

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Introduction

When a partially filled batch reactor undergoes an uncontrolled exothermic reaction, several things occur simultaneously. Heat, created by a chemical reaction, warms the content, producing a temperature and pressure rise. The reaction changes the composition, converting reactants into reaction products and byproducts. As temperature rises, the rate of chemical conversion accelerates. Eventually, reactor pressure reaches the set pressure of a relieving device, which then opens. The relieving flow rate is not a constant value, but changes with the reactor inventory, composition, pressure, temperature, and the limitations of the relief system.

The problem is to find a method for sizing the relief system that models these factors. Ideally, the method used should provide suitable information for safe sizing of the relief device, the related piping, and any downstream separation or recovery equipment. An article just published in "Chemical Engineering Progress of March, 1995, pages 33 to 43, shows the detailed description of a recent reactor design project and illustrates the need for using an integrated approach to calculating the required information.

The reaction uses a two-stage batch process, in which the reactants are mixed with a heavy solvent and water. This multi-component system produces a slurry containing product and byproducts. Heating initiates and accelerates the reaction in the agitated vessel. The reaction is under temperature control by means of a tempered external cooling system. The first stage reaction occurs well below the rector design temperature and pressure, during which more than 80% of the reactants are consumed. After an injection of water to the reactor, the second reaction takes place at a higher temperature and pressure, which drives the reaction to near completion in a reasonable time of several hours.

The effect of a runaway reaction are highest during the first reaction stage, when most of the reactants have not been converted. As with most reactions, the kinetics slow as reactants have not been converted. As with most reactions, the kinetics slow as reactant concentrations fall. Consequently, the two-stage reaction operation was developed. Because the reaction is very exothermic, a possible runaway situation might be initiated by a loss of reactor cooling.

Figure A shows the pressure relieving devices and their arrangement with inlet piping at the reactor top.

In this final plant design, two relief device systems protect the reactor. The first consists of two rupture discs in series to provide high pressure protection at all times. The second system consists of one pressure safety valve, set at a lower pressure to protect the system during the low pressure reaction stage.

The reactor piping design includes a block valve between the reactor and the pressure safety valve, allowing isolation from the reactor during the second stage reaction. Use of this pressure safety valve minimizes the venting rate and thus the product losses that a runaway reaction would create during the first reaction stage, if the rupture discs were the only protection.

Figure B shows adiabatic simulation curves for temperature and pressure rises as function of time during a reactor runaway situation.

These adiabatic simulation curves were calculated with client given input data for the kinetic reaction equation, using Wilson Activity Coefficients for the components of the reactor content in order to obtain the reactor pressures at every time step. These curves, thus calculated, matched client observed data.

These curves show that the relief valves set pressure of 125 psig could be reached at 429°F, the rupture disc bursting pressure of 350 psig at 552°F and the reactor MAWP 545°F.

The time interval to reach the above pressures and temperatures from the assumed reaction starting temperature of 375°F by self-propagated reaction without cooling is about 37.1 minutes, 46.6 minutes and 47.1 minutes, respectively.

After this introduction, the interested reader is advised to consult the main article for details.

The article shows graphs with comparative relieving rates for the different safety valve sizes and rupture disc sizes as a function of set pressures and relieving time intervals for vapor relief, if complete phase separation in the reactor top can be assumed. They also show additional graphs for flashing homogeneous two-phase relief flow, if phase separation in the reactor top is excluded.

Because of time limitation, only an abridged explanation of the tables and figures from the main article is given during this presentation.

FIGURE A

REACTOR PRESSURE RELIEVING DEVICES

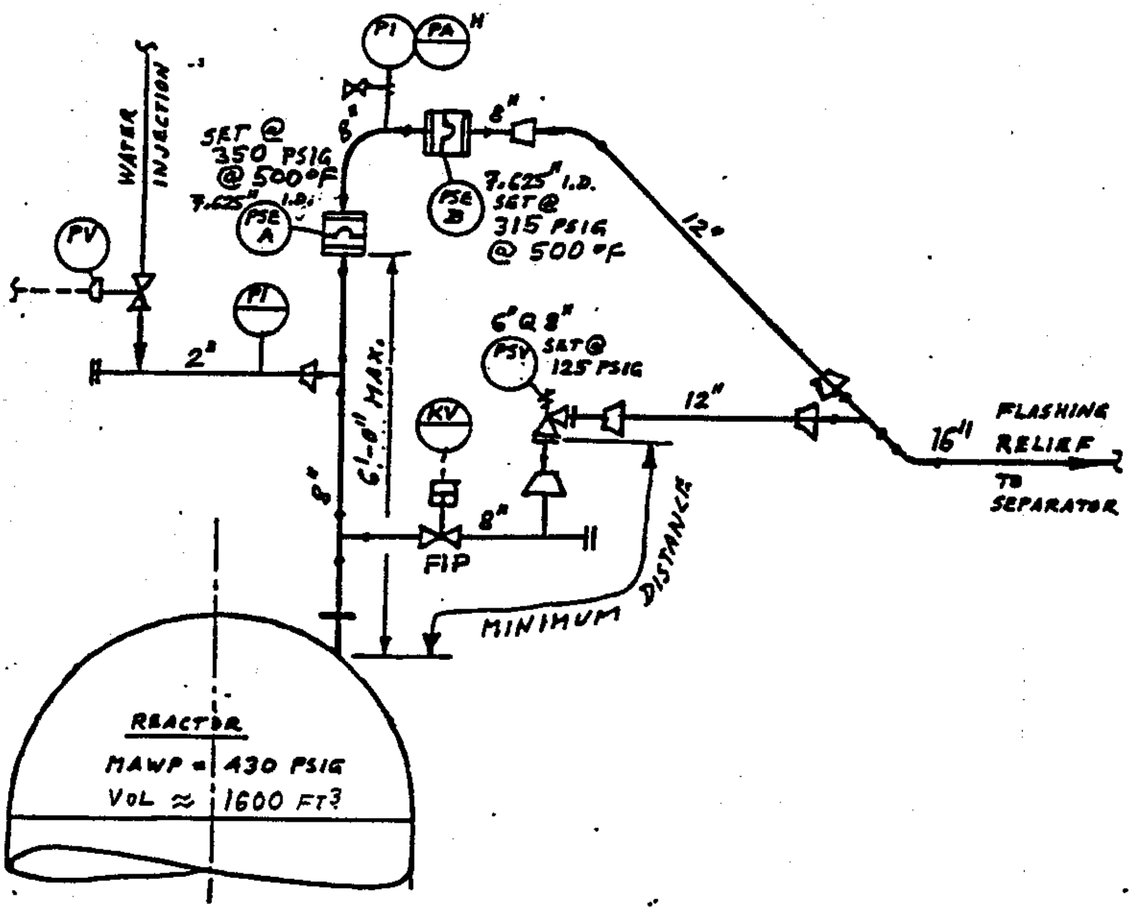
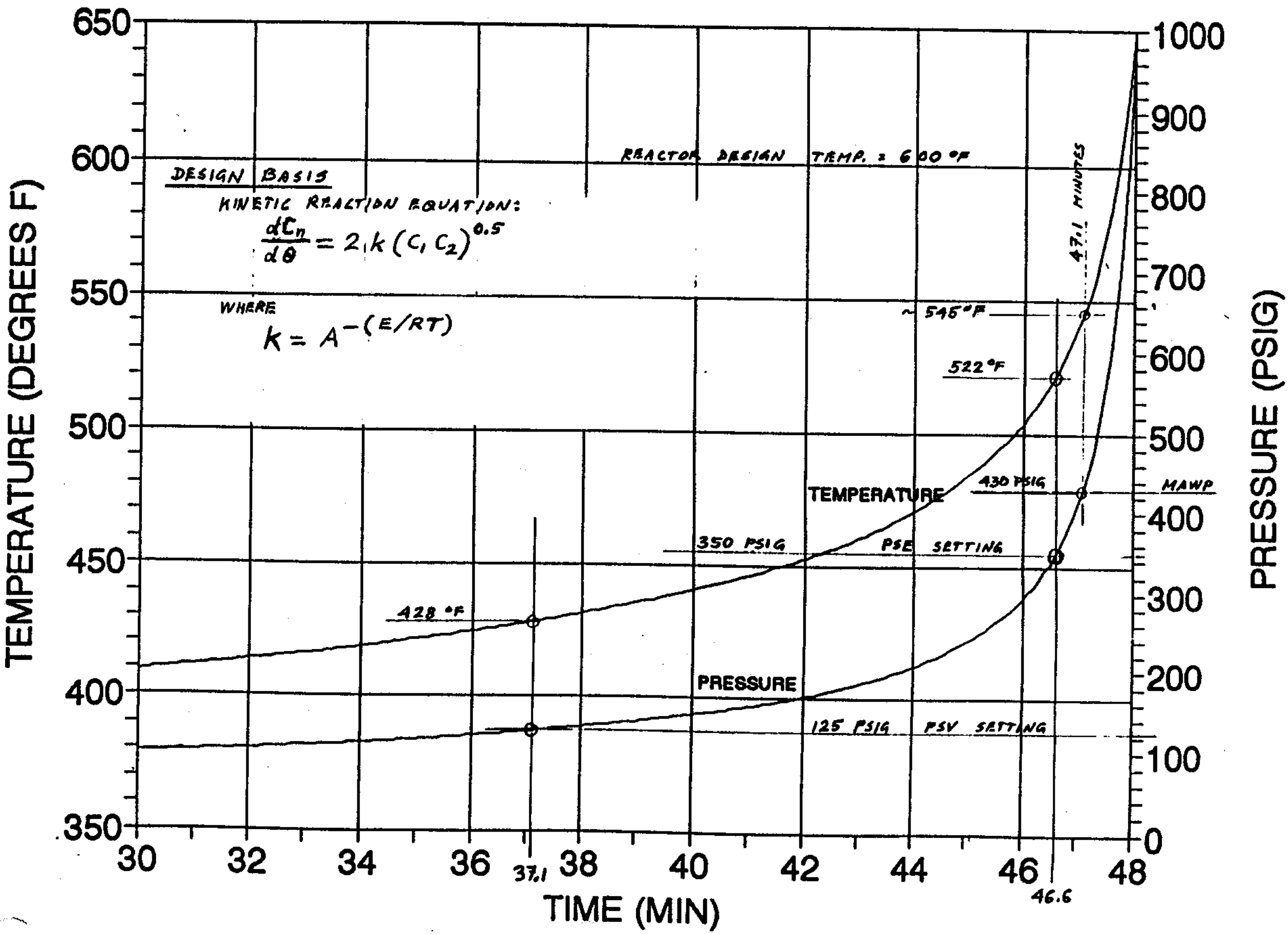


FIGURE B

ADIABATIC SIMULATION



"Accurately Size Batch Reactor Relief Systems," by Frank Turner and Siegfried H. Richter, *Chemical Engineering Progress*, Vol. 91, No. 3, pp. 33-43 (1995)

Accurately Size Batch Reactor Relief Systems

During a chemical reaction, the relieving flow rate is not constant, but varies with factors such as reactor inventory, pressure, and temperature.

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Relief valves and rupture discs are common devices that protect process equipment from damage due to overpressure. Sizing a relief valve or rupture disc is not difficult for most nonreactive applications, once the engineer determines which cause of overpressure produces the largest relieving rate. However, when the vessel's contents undergo a chemical reaction, calculating and deciding upon the sizing basis for a relief device becomes far more complex.

When a partially filled batch reactor undergoes an uncontrolled exothermic reaction, several things occur simultaneously. The heat of reaction warms the contents and both temperature and pressure rise. The reaction changes the composition in the reactor, converting reactants into products and byproducts. As the temperature rises, the rate of chemical conversion accelerates. Eventually, the reactor pressure reaches the set pressure of the relieving device, which then opens. The relieving flow rate is not constant, but changes with the reactor inventory, composition, pressure, temperature, and the limitations of the relief system.

The problem is to find a method for sizing the relief system that models these factors. Ideally, the method used should provide suitable information for safe sizing of the relief device or rupture disc, related piping, and any downstream separation or recovery equipment. This article describes a procedure for generating computer programs that simulate runaway reactions. A recent reactor design project is used to illustrate the process, demonstrating the need for using an integrated approach.

Traditional relief device sizing

Vendor literature, the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code, and American Petroleum Institute (API) standards provide a traditional approach to sizing relief valves and rupture discs. With this approach, the engineer estimates the required discharge rate and selects a valve model and size that has a capacity larger than the needed flow rate, given the relieving temperature, pressure, and composition. This method is acceptable for most nonreactive systems, but can grossly oversimplify the situation for a reactor. The accuracy of this method is even more uncertain when two-phase flow occurs during venting.

When using the traditional method to size a relief device for a reactive system, the engineer typically makes several implied assumptions. First, the peak relieving rate occurs immediately after opening of the relief valve or bursting of the rupture disc. Second, this peak venting rate is not affected by changing composition. Third, the relief device operates independent of any influence from the physical piping installation. Each of these assumptions can be incorrect, as will be discussed.

Required information

In preparation for design of the reactor relief system, a considerable amount of information must be assembled. This is true whether using a commercial relief-system program such as AIChE's SAFIRE or when developing a simulation program internally. Any assumptions made during the collection of information could have significant impact on the suitability of the final design and must be considered carefully. Some analytical testing may be required to generate the necessary information. The following section describes some of the design considerations and types of information which are required for simulating a batch reactor relief system.

Relief system design

Design of the relief system should be performed as early in the design phase of a project as possible. The large flows which may be produced in a relieving situation can result in large-diameter lines, vapor/liquid separators, and vent stacks. Allowing the plant layout to become finalized before designing the relief system makes redesign of nearby systems an unwelcome possibility. Large pressure drops in the discharge header and the methods needed to deal with the reactor discharge can result in relocation of the reactor. In some plant designs, the need to relieve a reactor safely has resulted in complete redesign of the reactor structure. Problems of this nature can be minimized by early design of the relief system. Minor process or layout changes can be resimulated as part of finalizing the detailed design.

In general practice, the relief valve or rupture disc is located at a minimum distance from the reactor, often mounted directly on a reactor nozzle. The selection of either a relief valve or rupture disc is made by the designer based on process considerations. Discharge piping should be kept as short as possible, leading to a discharge point suitable for the system. As the computer program uses a method that depends upon knowing the equivalent length of piping between the reactor and the relief device, this piping configuration must be fixed before the calculations can be begun.

Preliminary line sizing is adequate, as the impact of line size should be studied during the detailed design. Approximate equivalent length of a rupture disc holder with burst disc must be obtained from the rupture disc vendor. Equivalent length values for fully open relief valves are harder to obtain. DIERS uses an isentropic nozzle in its modeling of relief valves in the SAFIRE program. Discharge line routing downstream of the relief valve or rupture disc is also important, but not critical to the calculations. (This assumes that critical flow is forced by system design to occur at the discharge of the relief device, as will be discussed later.)

The volume of the reactor and ancillary equipment is required. If liquid entrainment is assumed, then the entire volume of the reactor system can be considered to be full of foam. This might extend into any overhead condenser, depending upon the location of the relief device.

The methods for disengagement of entrained liquid and discharge of vent gases must be given consideration. The computer simulation of the reactor produces information that will allow final sizing of the equipment and piping, but preliminary location of a knockout pot and suitable venting point must be made early in the plant design. These considerations are particularly important for flammable or toxic systems and when solids, high-melting-point material (polymers), or viscous material is discharged.

Chemical and physical properties

For each chemical in the reactor, certain basic information will be required. This list includes molecular weight, specific heat of vapor and liquid, latent heat, vapor and liquid viscosity, and liquid specific gravity. All pure-component properties should be available as functions of temperature, which may change significantly during the simulated runaway reaction.

Adiabatic vapor/liquid equilibrium calculations are a critical part of these simulations. At high pressure, vapor/liquid equilibrium will probably not follow ideal gas law K-values. Use of an equation of state to account for pressure effects on vapor/liquid equilibrium will need to be considered. Activity coefficient information may also be required to account for nonideal liquid-phase mixtures. The methods used should be able to account for any inert or nonvolatile components which may be present.

Reaction kinetics will need to be estimated over a wide range of conditions. The effects of changing temperature, pressure, and composition will have to be calculated during program execution. Any side reactions or competing reactions must be considered. For instance, significant degradation of a chemical at high temperature into volatile components could seriously affect the calculated relieving rates and operating conditions.

The venting characteristics of the system, if known, should be considered. Does the system foam, contain surfactants, operate as a slurry, or have significant viscosity? If so, liquid entrainment is likely during relieving. When in doubt, the design engineer should assume liquid entrainment for plant design.

Operation

A detailed understanding of the batch process is essential. Knowing the sequence of chemical addition, rate of addition, temperature, and pressure during each stage, and equipment used during each step allow a more accurate simulation of the runaway reaction.

For example, a reaction which begins as a final ingredient is slowly added should be considered to begin during the ingredient addition. Loss of electrical power, possibly stopping agitation and reactor cooling, would have slight impact if very little of the last reactant has been added. This same loss of power at the end of the reactant addition might result in a runaway reaction, but the predicted composition of the batch should take into account the partial reaction which took place during the addition of the final reactant. In the example project. the initial conditions were found to have a significant impact on the maximum venting rates.

The design engineer should also consider simulating upset conditions, such as over- or undercharging of any component. If manual addition is used in a batch, complete omission of an ingredient or a double charge might be conceivable. Imagine the effect of a double charge of catalyst on a reactor.

Simulation model

Having assembled the information described above, the design engineer must establish a credible scenario resulting in reactor relief. When necessary, several scenarios should be studied to ensure that the plant design covers the worst-case situation. In considering each scenario, the engineer should consider the entire situation, as some situations produce indirect effects which can worsen the relieving rate. Consider the following examples:

A reactor might experience a runaway reaction if electrical power to the plant is lost, stopping the agitator and cooling-jacket circulation pumps. If the power outage is assumed to occur at the point when the batch is at its highest level of reactants, one basis for calculation can be developed. If the power outage is assumed to be local, caused by damage due to a fire external to the reactor, then heat input from fire might also be considered. Fire was not considered significant in the example plant since the reactor had a heat-transfer-fluid filled jacket and heavy insulation, and was protected by a fire sprinkler system.

Consider a reactor designed with internal cooling coils or an external jacket. The engineer must consider if the scenario should assume heating of the vessel walls and jacket coolant. The example project had a reactor which used both an internal coil and external jacket for cooling. Loss of power to the agitator and buildup of thick slurry along the reactor wall and coil was thought to limit heat transfer to the reactor vessel wall during the several minutes needed for the reactor to empty during a runaway. The calculations conservatively ignored heat pickup by the vessel and jacket fluid.

A double charge of catalyst to a batch would probably not result in loss of agitation or jacket cooling. This scenario should then assume cooling occurs normally, building to the design cooling rate of the cooling system during a runaway. Assuming a double charge of catalyst and simultaneous failure of power, for instance, probably would be considered too unlikely a double jeopardy.

A final consideration is whether or not to assume liquid entrainment. Entrainment was known to occur in the design example and was modeled as a uniform froth. Visualize a reactor pressurized with shaving cream and allowed to vent: the froth is initially very rich, high in liquid phase. As the contents of the reactor empty, the liquid-phase portion of the foam decreases. At the end of the reaction, the proportion of liquid to vapor phase is at its lowest value. Because the vessel is assumed to stay full of foam, there is no time when only vapor is relieved.

Other estimates of liquid entrainment are given as options in the SAFIRE program from DIERS, but choosing among them should be based on some knowledge of the actual reactor system.

> *The design engineer must establish a credible scenario resulting in reactor relief*

Optimization of the programs

Because of the complexity of these programs and the huge number of repetitive calculations performed, the computer system used should have either a 486 or Pentium processor. Use of a compiled language package should also be regarded as mandatory. Choice of language is left to the engineer. The work done on the example project was done using a 486-33 computer and Borland C++ (using C source code). Execution times could run over an hour. The methods used were not optimized for speed, but were chosen to reliably converge on real solutions.

As described, the programs operated as a series of nested calculations. This arrangement is the coding algorithm most likely to converge, the easiest to code, and the simplest to logically visualize. The shortcoming of such an approach is long execution times.

In performing each adiabatic flash, simultaneous solution of several nonlinear equations would shorten the program execution. This option was not explored as a discontinuity in the heat balance formula exists at the pressure where the relief valve opens and closes, or the rupture disc bursts. Such a discontinuity might make convergence difficult. If the engineer has time to explore options, this might significantly reduce the execution time of the program.

In theory, all of the nested loop calculations could be solved simultaneously by nonlinear matrix methods. This approach would involve significantly more complex programming and debugging than the programs developed for the sample project, but should substantially reduce execution time. Since these programs are typically designed only for one plant or process, high program speed should be considered a lower priority than avoiding a lengthy programming and testing exercise. Commercial programs like SAFIRE may have been optimized along these lines.

All variables were defined as double precision. This allows use of very small convergence values for each iterative calculation. If the allowed convergence error values were too coarse for reactor pressure, adiabatic flash temperature at known pressure, and fraction of vapor formed in each vapor/liquid equilibrium, the programs might not adequately converge on an accurate solution in each time period. This could be detected by plotting flow vs. time. The changes in flow, once the rupture disc bursts or a relief valve opens, should result in a smooth curve. If such a plot has a cyclic or wavy appearance, the convergence criteria are too coarse.

Example: reactor operation and design

This example uses a two-stage batch process, in which the reactants are mixed with a heavy organic solvent and water. This multicomponent system produces a slurry containing both product and reaction byproducts. Heating initiates and accelerates the reaction in an agitated vessel, and the reaction is under temperature control by means of a tempered external cooling system.

The first reaction stage occurs at about 430°F and below 100 psig, during which more than 80% of the reactants are consumed. These operating conditions produce a controllable reaction rate and are well below the reactor design temperature and pressure. After an injection of water into the reactor, the second reaction stage takes place at 490°F and 250 psig. These operating conditions drive the reaction to near completion in a reasonable time of several hours.

The effects of a runaway reaction are highest during the first reaction stage, when most of the reactants have not been converted. As with most reactions, the kinetics slow as reactant concentrations fall. Consequently, the two-stage reaction operation was developed. Because the reaction is highly exothermic, a possible runaway situation might be initiated by a loss of reactor cooling. Loss of cooling could have several causes, including control failure, electrical failure, and cooling-water failure.

The reactor is a closed vertical vessel, with system pressure set by the vapor pressure of the vessel contents. The vessel is designed for 430 psig and 600°F with a two-speed agitator. Heat transfer is via a tempered, recirculated heat-transfer fluid, using an internal coil and an external jacket.

In the final plant design, two relief device systems protect the reactor. The first consists of two rupture discs, set in series, to provide high-pressure protection. Two rupture discs in series were chosen to provide a safeguard against loss of the batch due to corrosion or fatigue of the first disc.

The second system consists of one pressure safety valve, set for 125 psig, to protect the system during the low-pressure reaction stage. The reactor piping design includes a block valve between the reactor and the pressure safety valve, allowing isolation from the reactor during the second stage reaction. Use of a pressure safety valve minimizes the venting rate that a runaway reaction would create during the first reaction stage. Computer simulation of this system shows that relieving at 125 psig would have a peak mass-flow rate about 10% of the maximum rate expected through the two rupture discs at 350 psig.

Because the organic solvent has an open-cup flash-point temperature of 7°F, any release to atmosphere could result in a fire or explosion. To minimize this possibility and also consequent cleanup problems, the relief valve and rupture discs are connected to a knockout drum, from which a vent stack releases escaping vapor above the plant structure.

Reaction kinetics and physical considerations

The reaction occurs with the following kinetic formula:

$$dC_n/d\theta = 2k(C_1C_2)^{0.5}$$

where: $k = A\ \exp(-E/RT)$; A = frequency factor; C_n = byproduct concentration at time θ; C_1 = Reactant 1 concentration at time θ; C_2 = Reactant 2 concentration at time θ; E = energy of activation; k = reaction constant; R = gas constant; T = reactor temperature; and θ = reaction time.

The reaction kinetics are thus considered dependent on temperature and liquid-phase concentrations, but independent of system pressure. This formula is assumed valid to near completion and at all reactant concentrations.

Batch composition is significant only in that water in the liquid phase is present in a small concentration compared to the organic solvent. Water is the most volatile chemical present, and the organic solvent is lower in volatility. All reactants are intermediate in volatility and the reaction products are nonvolatile.

Wilson equation activity coefficients compensate for liquid-phase nonideality for water, the organic solvent, and one of the reactants. Because coefficients were not available for the remaining reactant, ideality was assumed. The resulting calculated vapor pressure at different temperatures closely matched data provided by the licensor. Consequently, vapor-phase ideality was assumed, eliminating the need to use an equation of state in the simulation.

General approach

A computer program was unavailable that would both rigorously model the reactor system and handle time-dependent vapor/liquid/solid multicomponent equilibria in the reactor and through the relief vent system. Significant liquid losses occurred during discharge from a low-pressure relief valve on a similar plant; this aggravated the problem. Any program used for these calculations must include an accurate method for two-phase flow. Some programs exist for modeling multicomponent unsteady-state systems, but were unavailable for use or review. Consequently, John Brown developed the programs used for the reactor relief system design.

The computer programs simulate the batch during short time increments of 0.1 min. Different time intervals were tried on preliminary computer runs. Increments of 1.0 min resulted in only approximate solutions, due to the short relieving time. Time intervals of 0.1 min produced a reasonable number of data points, allowing for an accurate simulation of changing reactor conditions and mass-flow rates during venting.

Table 1. Equivalent length for rupture-disc assemblies.

Nominal Rupture Disc, in.		8	
Choke Tube Dia. = Throat Dia., in.		7.625	
L/D for One Blown Disc	75 max	30 min	75 max
Choke Tube Equivalent Length,			
Without Acceleration Loss, ft	97	53	87
Inlet Acceleration Loss, ft	24	24	17
Total Equivalent Length, ft	121	77	[illegible]

Table 2. Area and pseudo diameter for safety valves.

Safety Valve Size	Orifice Size	Orifice Area, in.^{2}	Pseudo Orifice [illegible]
4P6	P	6.38	[illegible]
[illegible]	Q	11.05	[illegible]

Increments of 0.01 min resulted in reactor operating conditions and venting rates similar to the 0.1 min increment, but required much more time per calculation. Within each interval, the rate of reaction was calculated using the reactant concentrations and temperature from the previous interval. Preceding relieving, the heat of reaction results in a temperature and pressure rise. This temperature is calculated by trial and error within the program, such that the sensible heat used in the temperature rise must balance the heat released by the reaction. The chemical composition is revised to reflect the chemical conversion during the interval, and the saturation pressure is calculated.

When the calculated pressure exceeds the set point pressure of the relief valve or the burst pressure of the rupture disc, venting begins. Several relieving scenarios were modeled for both rupture discs and relief valves, assuming either vapor flow or a homogeneous two-phase froth.

For simulation purposes, the batch runaway reaction was assumed to occur totally adiabatically. Electrical failure in the plant would approximate this condition, as jacket cooling and batch agitation would be lost.These calculations ignore heat transfer to the reactor steel and jacket oil, since the presumed loss of agitation would limit heat transfer. The assumption of adiabatic operation is considered a conservative choice, since any actual heat absorbed by the reactor steel and jacket oil would lengthen the time to onset of venting and lessen the consequent venting flow rate.

Venting from a reactor could be modeled in several ways. One approach is to simulate a rupture disc or a relief valve as a simple orifice, but this approach does not recognize pressure losses in the piping upstream and downstream of the relieving device. In our plant design, the rupture disc assembly, consisting of two rupture discs with holders separated by an elbow, has 6 ft of vertical pipe between the reactor and the primary rupture disc. This assembly was modeled as a choke tube with an inside diameter equal to the interior diameter of the rupture disc holder. Choke tube equivalent length was calculated from the resistance coefficients of each pipe component following Crane's Technical Paper 410, "Flow of Fluids Through Valves, Fittings, and Pipes."

Using equivalent length ratios provided by a rupture disc vendor, the choke tubes modeled for the rupture disc assemblies resulted in the dimensions given in Table 1.

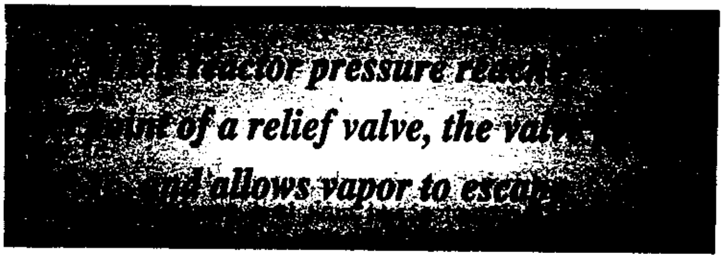
Critical flow exists at the exit of the choke tube when the built-up downstream backpressure is below the critical flow outlet pressure of the material traveling through the choke tube. This is guaranteed by proper design of the discharge piping and equipment downstream of the second rupture disc, using the peak flow rates predicted by the programs we created. In the project, 12-in. pipe was used for the discharge header to prevent overpressure of the low-pressure relief valve.

Conceptually, an open pressure-relief valve could be modeled similarly. Although conventional sizing equations treat a relief valve as an orifice, several coefficients factor into the equation to make the predicted flow conform to laboratory test results. This approach has proven accurate for single-phase vapor or liquid flow.

In any detailed simulation involving pressure relief valves, any fluid traveling through the valve must follow a tortuous path. A conventional relief valve contains three or more throat areas that are connected in series, each of fixed or variable size. These throats include the inlet nozzle below the disc, the area between the seating surface and the moving relief valve disc, the huddling chamber formed between an adjusting ring and the disc skirt, and the outlet nozzle. In addition, between these areas of restricted flow there are direction changes, contractions, and expansions through which any fluid must travel. Because of these factors, each type of relief valve has different flow characteristics. Disc lift limiters, ring adjustment, spring adjustment, and variable overpressure below the disc serve to further complicate accurate modeling of relief valves.

For these calculations, it was assumed that the relief valve remained fully open during the entire relieving scenario. This assumption is valid when the relieving pressure exceeds the design overpressure (in this case 10% above the relief valve set pressure per API for non-fire situations). We further assumed the governing throat area to be the same size as the nominal relief valve orifice area. The resulting data are in Table 2.

Assuming that a fully open relief valve can be modeled as a choke tube, the choke tube inside diameter was set equal to the diameter of the relief valve orifice, with a L/D of 175. To account for inlet piping and fluid acceleration losses, another L/D ratio of 80 was added. Thus, the total equivalent length of a relief valve was assumed to be: $L = 255D$. This is only a preliminary estimate and preferably should be confirmed by the vendor or by independent testing. In our case, extensive testing was judged not to be required because the reactor was ultimately protected against overpressure by the rupture disc assembly. Overpressure above 110% of the safety-valve set pressure due to underestimation of the equivalent length would not endanger reactor safety.



When a rupture disc or a relief valve is modeled as a choke tube, the reactor pressure is variable. Material leaves the reactor at a rate that is affected by the pressure drop in the discharge system. With a runaway reaction, the most likely limitation is reaching critical flow at some pinch point in the system, such as at the second rupture disc holder or the relief valve.

If modeling only vapor, compressible-gas-phase formulas are suitable for calculating reactor pressure from the downstream point where the gas velocity becomes sonic, knowing the equivalent length of the line between the reactor and the relief device. The downstream vapor line, separation system, and stack would therefore have to be designed not to produce backpressure high enough to affect the formation of sonic flow at this constriction.

When two-phase flow is assumed, the calculations are more involved. As pressure drops in passing through a pipe, the amount of vapor increases due to partial flashing of the liquid. This results in a variable pressure drop per foot of equivalent length.

Reference 1 describes a method for modeling such a system (see Reference 2 for background information). Simply described, for each time increment the procedure starts out by calculating the critical-flow outlet pressure at the pinch point for gas and liquid leaving the reactor at an assumed reactor pressure. The article includes a formula for calculating the equivalent length of pipe that produces a certain pressure drop, say 1 psi. Using this method with small pressure steps allows calculation of line pressure drop from the relief device backwards to the reactor, providing a check on the assumed reactor pressure. If the assumed and calculated reactor pressures do not agree, a new reactor pressure is assumed and the calculations repeated. The method also permits adjustment of both gas- and liquid-phase quantities, along with their physical properties, for the pressure found in each equivalent length increment. This is a significant departure from normal shortcut or two-phase pressure drop procedures.

This results in a trial-and-error calculation, searching for an assumed reactor pressure in each time increment that would produce the correct amount of vapor and liquid needed for critical flow in the exit of the choke tube.

There are several advantages to performing these calculations, which are not performed with any known shortcut method for sizing relief valves or rupture discs. The first is having a means to develop a rational basis for the system design, reflecting the most demanding scenario being considered. A second one is, for each time increment, knowing in detail the flow rate and composition of material to be handled by any downstream knockout drums or recovery systems. An additional advantage is knowing the reactor conditions when the reaction ends.

Relief valve simulations

Constant pressure simulations, single-phase venting — When reactor pressure reaches the set point of a relief valve, the valve opens and allows vapor to escape. This flow may be two-phase. When not undersized, the relief valve theoretically can maintain a constant vessel pressure by throttling the flow. If grossly oversized, the valve would vent more vapor than the batch is creating, causing reactor pressure to fall. As the pressure drops below the set point pressure, the relief valve would reseat and stop venting until pressure rises to the set point pressure again.

The program makes an adiabatic flash calculation at a specified reactor pressure. This calculation figures out the resulting vapor rate/composition and batch temperature, such that the sensible and latent heat changes equal the heat produced by the reaction. The program revises the chemical composition at the end of each time increment to reflect the chemical conversion and venting losses. Calculated reactor temperature and pressure, along with the quantity and composition of the vented material, are stored in a file for later design of downstream equipment. Program operation continues until a reactant is exhausted.

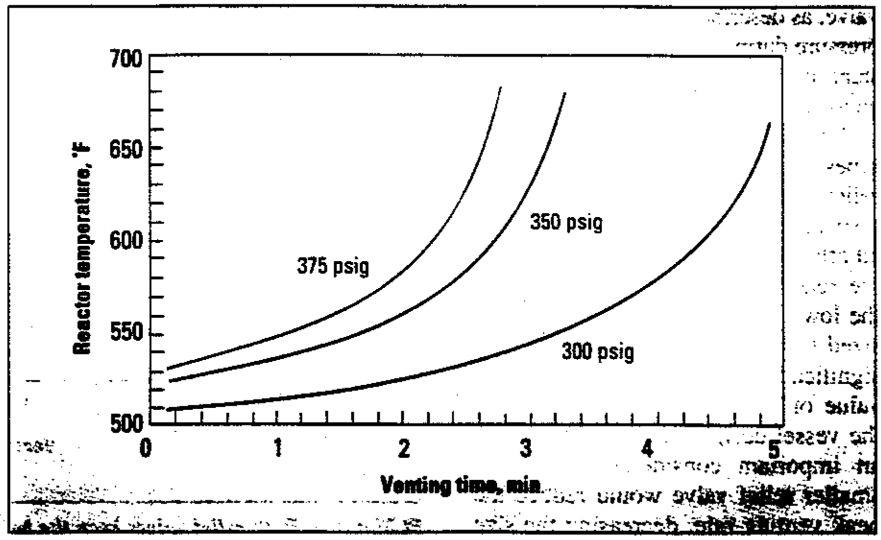
Initial simulations focused on operation of a 4P6 pressure relief valve and assumed only vapor venting. Figure 1 shows plots of reactor temperature against time for several pressure safety valve (PSV) set point values. For each set-point pressure case, the reactor temperature rose during venting and exceeded the design temperature of the vessel. In fact, this temperature rise exceeded the temperature limit possible for carbon steel, 650°F even when set pressures were reduced to pressures only slightly above the second stage reaction pressure. A larger size relief valve would not reach the maximum vessel temperature limit.

Clearly, finding results like this would not have been possible using any shortcut procedure. This ability is particularly important when the vessel walls are made of dissimilar materials, such as clad metal or glass-lined steel. The high-pressure relief valve design was replaced with the dual rupture disc arrangement described earlier.

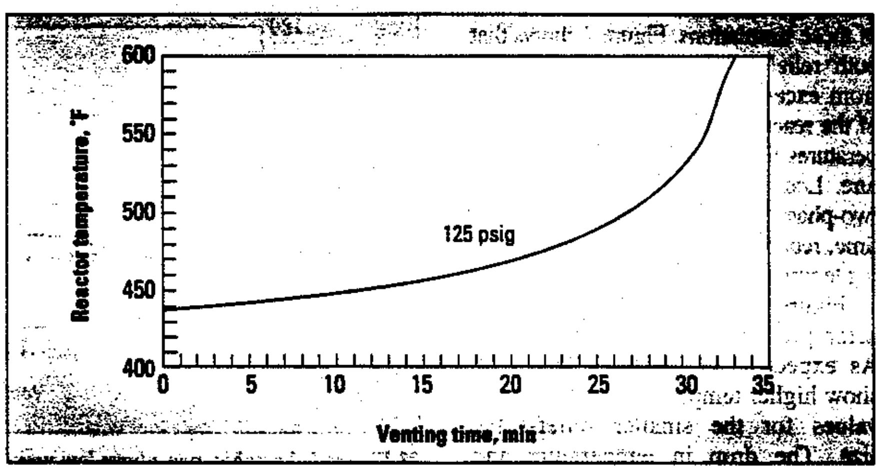
Repeating these calculations for the low-pressure relief valve produced the temperature plot shown on Figure 2. The temperature does not exceed 650°F making use of a relief valve for low-pressure relief an acceptable design. Figure 3 shows the vapor rate leaving the low-pressure relief valve. Both temperature and venting rate increase as time passes, results which would invalidate any relief valve design based on initial venting estimates.

Initially, for first stage reaction at low pressure, the vent gas has a high proportion of water, with smaller amounts of reactants and solvent. Increasing temperature and flow rate are probably due to the rising concentration of heavy solvent in the reactor. The organic solvent has a lower vapor pressure and latent heat than water. As the water leaves the reactor, the temperature is forced upward and greater amounts of organic solvent boil off to remove the heat of reaction. This increase in temperature also accelerates the reaction rate and vapor formation. The maximum venting rate occurs as the reaction dies due to a lack of reactants.

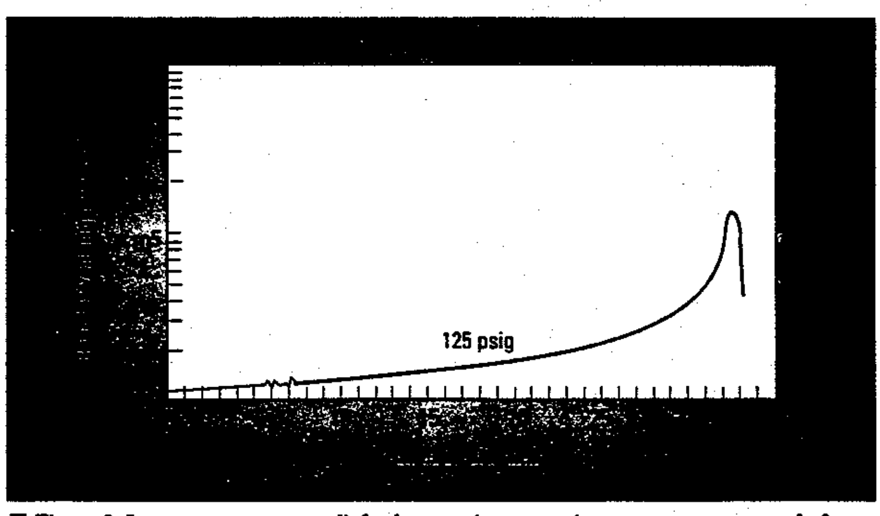
Variable-pressure simulation with flashing two-phase venting — Because two-phase venting is known to occur in this system, flashing flow simulations were run, assuming a homogeneous mixture of vapor and liquid in the reactor. With this scenario, the worst case flows occur when the relief valve is assumed to be completely open during the bulk of the reactor venting. The limiting case for discharge rate then would be critical flow in a choke tube modeling the relief



■ *Figure 1. For high-pressure process safety valve (PSV), temperatures exceed limit for carbon steel.*



■ *Figure 2. Low-pressure relief valve yields acceptable temperature rise.*



■ *Figure 3. Low-pressure vapor relief valve; maximum venting rate occurs near end of run.*

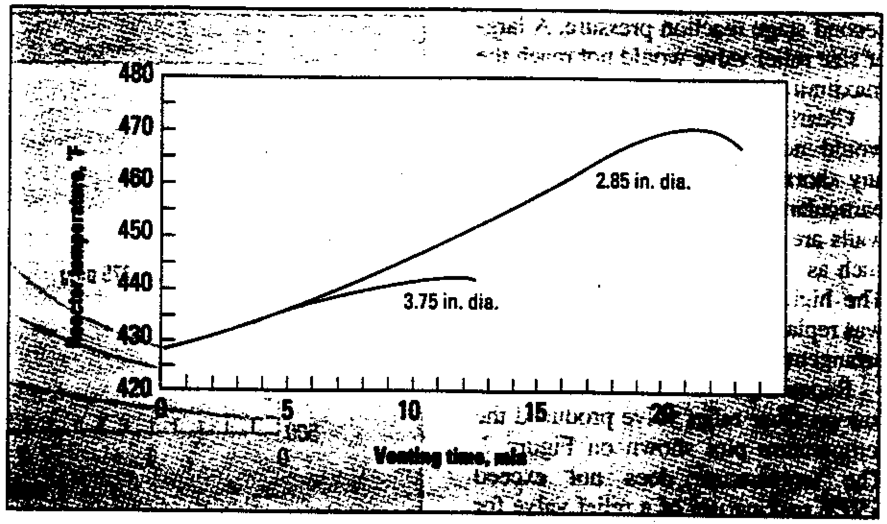
valve, as described above. Since reactor pressure during venting is not held constant, the design simulation is run with an assumed choke tube diameter.

Simulations were run using choke tubes with dia. of 2.85 and 3.75 in. for relief valves with 4- and 6-in. inlets, respectively. These sizes were selected after some preliminary trials. Since the reactor is designed for 430 psig, the low-pressure relief valve could be sized to allow reactor pressure to rise significantly above the initial set point value of 125 psig without exceeding the vessel design temperature. This is an important consideration, since a smaller relief valve would reduce the peak venting rate, decreasing the size and cost of downstream recovery and separation equipment.

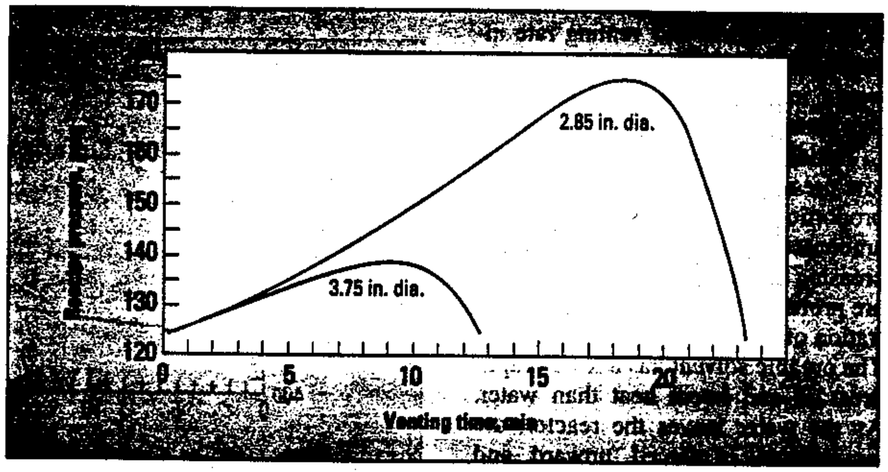
Figures 4, 5, and 6 show the results of these simulations. Figure 4 shows that both relief-valve sizes keep the batch from exceeding the design temperature of the reactor. These values peak at temperatures below the maximum temperature. Loss of reactants vented with the two-phase flow shortened the venting time, reducing the water loss and resulting temperature rise.

Figure 5 shows the calculated reactor pressure during relief venting. As expected, Figures 4 and 5 both show higher temperature and pressure values for the smaller relief-valve size. The drop in temperature and pressure at the right side of each curve is due to the exhausting of one reactant. Venting beyond the peak reflects adiabatic flashing of the reactor contents, with no heat of reaction.

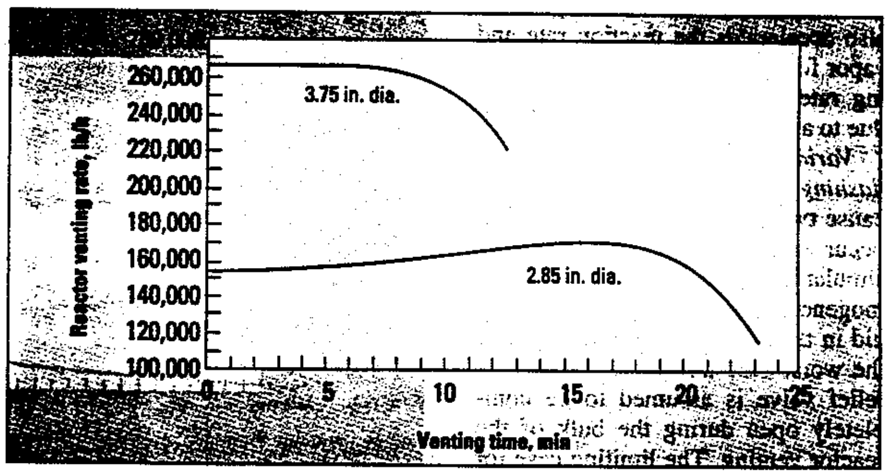
Figure 6 illustrates the venting rate from each relief-valve simulation. While the values are approximate due to uncertainties in the relief valve equivalent length, they do show a significantly larger venting rate than the vapor-only simulation. As expected, the smaller relief valve produces a lower venting rate and longer time for completion of the relieving event. These differences show that system design should include the effects of two-phase venting in any design. Traditional design methods do not allow such a



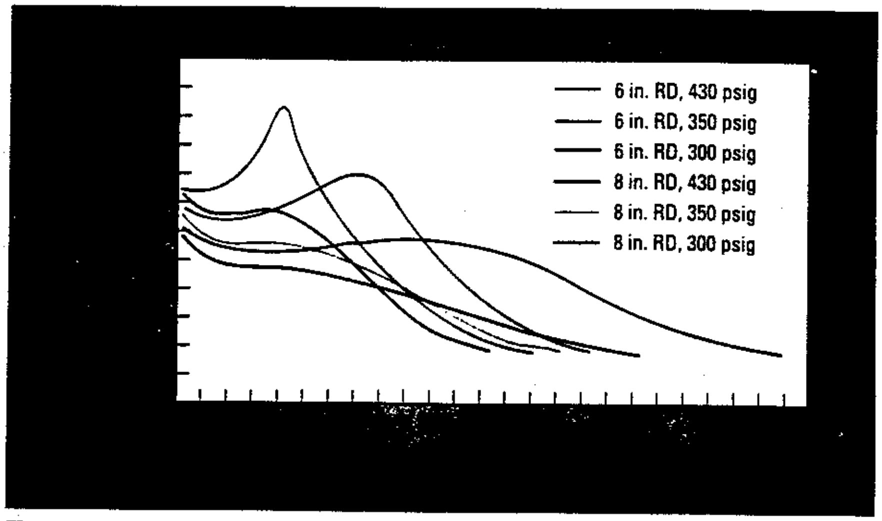
■ *Figure 4. Both relief valves keep the batch from exceeding the design temperature of the reactor.*



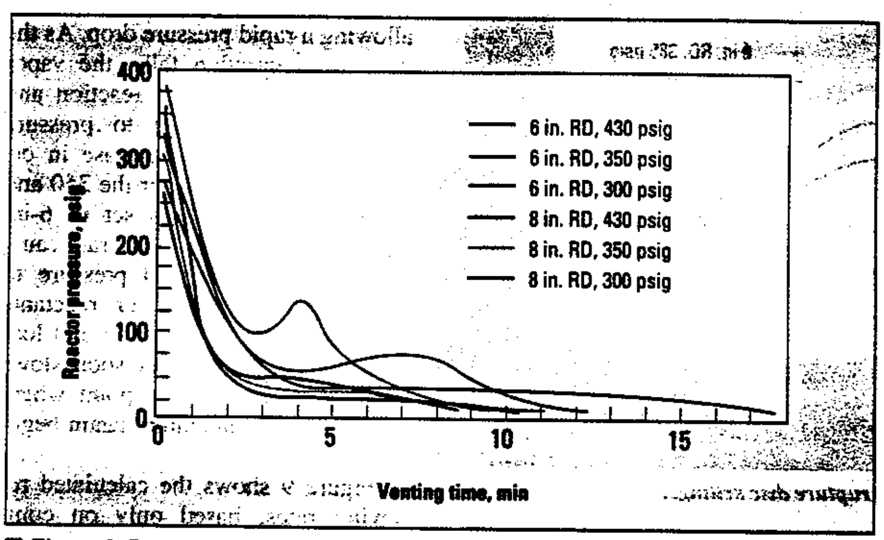
■ *Figure 5. Variable, two-phase low pressure; reactor pressure during relief venting reaches peak values.*



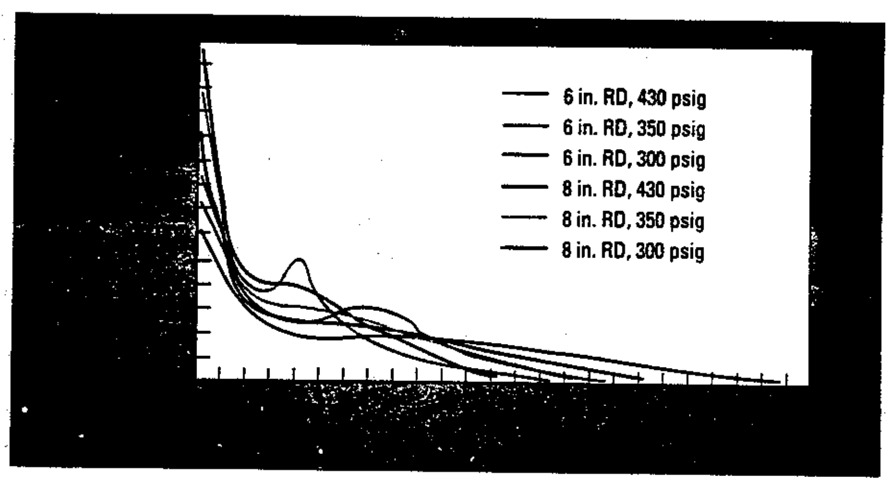
■ *Figure 6. Variable, two-phase low pressure; venting time varies with relief valve pseudo-diameter, back-calaculated from nominal orifice area.*



■ *Figure 7. Reactor temperature profiles for high-pressure venting, compressible gas.*



■ *Figure 8. Reactor pressure profiles for high-pressure venting, compressible gas.*



■ *Figure 9. Initial venting rates are different for each case, with 8-in. lines having significantly higher rates than 6-in. lines.*

calculation and would probably result in improperly sized separation equipment downstream of the relief valve.

Rupture disc simulation

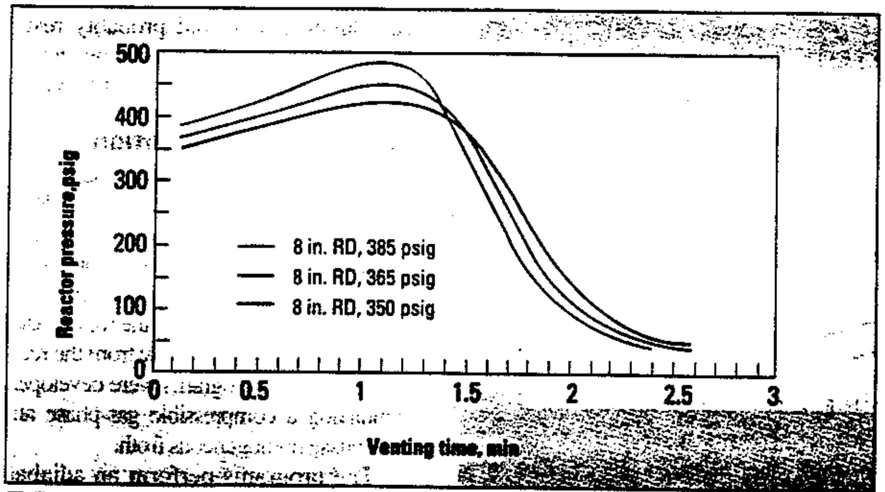
When reactor pressure reaches the burst pressure of a rupture disc (RD), vapor escapes from the reactor. As with relief valves, this vapor may be accompanied by significant amounts of liquid. The limiting factor is critical flow at the rupture-disc support, which restricts flow from the reactor. Two sets of programs were developed, simulating a compressible gas-phase and two-phase homogeneous froth.

The programs perform an adiabatic flash calculation at assumed reactor pressures. This calculation determines the batch temperature, vapor flow rate, ratio of gas to liquid in the vent stream, and chemical composition, such that the sensible and latent heat changes equal the heat produced by the reaction. Chemical composition is revised at the end of each short time increment to reflect the chemical conversion and venting losses. Calculated reactor temperature and pressure, along with the quantity and composition of the vented material, are stored in a file for later design of downstream equipment. The program ends when a reactant is exhausted.

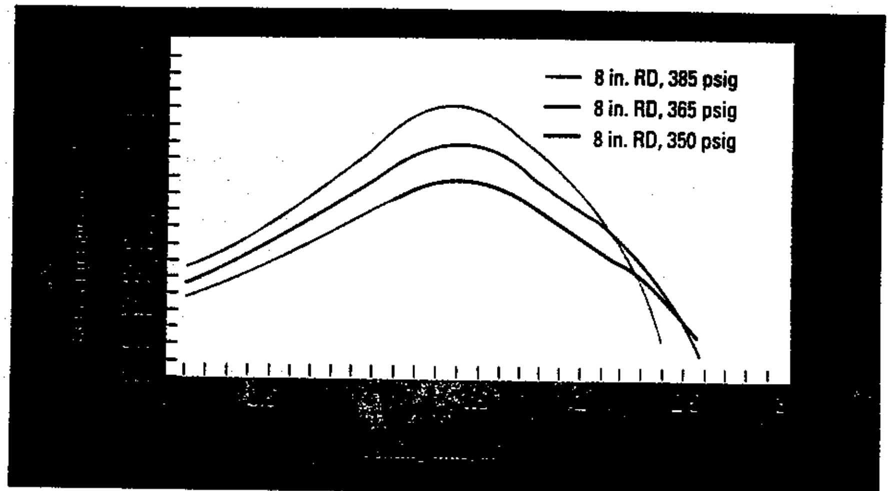
Compressible gas, single-phase venting

The program used for compressible gas-phase relieving is a simplification of the basic program used for two-phase relieving. The vapor discharge from the reactor, calculated at an assumed pressure, is used to calculate the sonic velocity at the rupture disc holder. Repeated calculation of the equivalent length in 1 psi increments allows a back calculation of the reactor pressure. If the back calculated pressure does not match the assumed reactor pressure, a new pressure is assumed and the calculations are repeated. These calculations were repeated for 6- and 8-in. rupture disc holders, assuming rupture disc set pressures of 300, 350, and 430 psig.

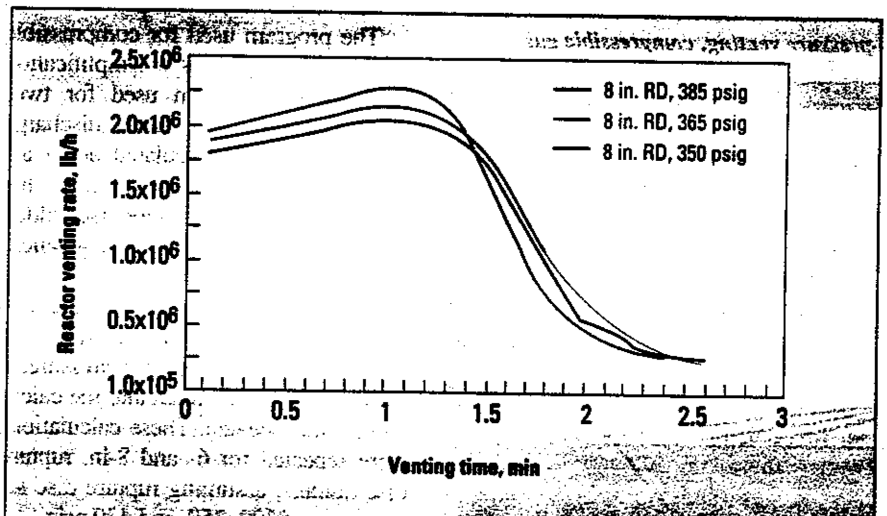
Figures 7, 8, and 9 show reactor temperature, pressure, and venting rate for



■ *Figure 10. Reactor pressure peaks roughly midway through the venting run.*



■ *Figure 11. Venting temperature for various rupture disc settings.*



■ *Figure 12. Reactor venting rate for flashing flow through rupture disc at various bursting ~~temperatures.~~* pressures.

each size and rupture disc burst pressure. While reactor pressure is no problem, Figure 7 shows that 6-in. rupture discs set at the reactor design pressure of 430 psig would result in the batch temperature briefly exceeding the coincident vessel design temperature of 600°F. Since reactor pressure is shown to have dropped to about 140 psig when this temperature is reached, this size could be considered acceptable if two-phase venting were not an issue. All other designs are more conservative.

The temperature and pressure peaks, calculated for the 6-in. rupture discs set at 350 and 430 psig, reflect changing kinetics and composition within the reactor. Initial vent gas has a relatively large proportion of water, allowing a rapid pressure drop. As the water concentration falls, the vapor rate set by the heat of reaction and adiabatic flashing due to pressure change results in an increase in organic solvent boilup. For the 350 and 430 psig rupture discs set in 6-in. lines, this increasing vapor rate causes the temperature and pressure to rise briefly. Depletion of reactants due to the ongoing reaction and loss with the relieving vapor soon slows the heat generated to a point where pressure and temperature again begin to fall.

Figure 9 shows the calculated relieving rates, based only on compressible vapor. Initial venting rates are different for each case, with 8-in. lines having significantly higher rates than 6-in. lines. Burst pressure was also significant in establishing peak venting rate. The higher the burst pressure, the larger the flow.

Compressible gas, with flashing two-phase venting

Relief through a rupture disc with two-phase flow was simulated using a program similar to the one employed for modeling low-pressure relief valves. The simulation was changed only to reflect the equivalent length of a choke tube based on the diameter of the rupture-disc holders and to continue calculation below the rupture-

Design of the equipment downstream of the rupture discs and relief valve is straightforward.

disc burst pressure. Rupture discs with a diameter of 8 in., the size of the reactor vent nozzle, were studied with set pressures of 350, 365, and 385 psig.

Two-phase flow greatly affects rupture disc relieving. Figures 10, 11, and 12 show reactor pressure, temperature, and relieving rate that increase after venting begins. A 385 psig rupture disc resulted in pressures of 490 psig and temperatures only slightly below the vessel design temperature. While an 8-in. rupture disc, set at 430 psig is acceptable for vapor relief in this system, flashing flow would result in exceeding both the design temperature and pressure of the vessel. This is a finding that would not be anticipated using traditional rupture-disc sizing methods.

Comparing Figures 9 and 12 shows that the relieving rate is considerably increased when flashing two-phase venting is considered. It should be noted that Figure 9 reflects a vapor stream, while Figure 12 shows a two-phase stream that is predominantly flashing liquid. Vapor rates leaving the reactor during two-phase venting are very low. Liquid chokes vapor flow by flashing. This phenomenon results in accumulated backpressure, producing the increase in reactor temperature and pressure. Discharge of much of the reactor batch as liquid, not chemical conversion, results in the eventual drop in reactor temperature and pressure.

Considering the uncertainties in these calculations, the final reactor design uses 8-in. rupture discs with a burst pressure of 350 psig.

Discharge piping, knockout tank, and discharge stack

Design of the equipment downstream of the rupture discs and relief valve is straightforward. The task is made easier in that the simulations have established a database of reactor discharge flows, temperatures, pressures, and compositions for each relieving condition. This information allows the engineer to calculate the percent flash at downstream system pressures. The resulting data permit stack sizing based on peak flash vapor rate and sizing of the relief system to prevent excessive backpressure. Vapor/liquid separators can be sized for the worst case of vapor and liquid flow. Thrust loading on the reactor relief discharge system can also be calculated.

Limitations

The only significant limitation is thought to be the lack of accurate choke-tube equivalent lengths for different rupture discs and relief valves. Given this limitation, simulation of rupture disc assemblies and relief valves as choke tubes is probably not unreasonable. Hydraulic flashing flow testing of relief valves by the manufacturer would be a considerable aid. CEP

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