Consider Bottom Venting for Reactive Liquids

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When a liquid in a vessel can undergo an exothermic runaway chemical reaction, bottom venting may provide safer and less expensive emergency relief than top venting. Here is how to evaluate these choices.

Most previous research, publications, and industrial practice have centered on top-venting pressure relief devices. These are popular because they offer a number of advantages for systems in which two-phase, vapor/liquid relief does not occur:

- Top-venting relief devices are easier to service, except on large columns or other tall vessels.
- Top-venting relief systems are more likely to retain liquid and vent only vapor; this extends the duration of protection during external fire exposure to a vessel due to the cooling effect of boiling liquid in the vessel.
- In many cases, the relieved fluid is a vapor that often can be released to the atmosphere at a safe elevation.
- Vapor-only relief events have relief rates that are an order of magnitude smaller than two-phase relief rates, and they do not discharge large masses of liquid; thus, relief header and treatment systems are smaller and less costly for top-venting.

However, when contained liquids undergo exothermic runaway chemical reactions, top venting systems may be large and thus costly, especially for larger process vessels. This is due to the extended duration of top venting relief, during which relief temperatures may rise significantly. Higher temperatures lead to much higher reaction rates, possibly leading to an unventable reaction. When very fast exotherms or chemical decomposition reactions are expected, then even a rupture disk with a diameter equal to the diameter of the vessel may fail to protect the system, and the runaway is said to be unventable. In these cases, either instrumented dump systems or passive bottom-venting relief (PBVR) systems may be the only safe options to protect the process vessel.

Bottom-venting emergency relief systems can remove energetic liquids from a process vessel much more rapidly than top-venting ones. Once removed, the liquids can either be quenched or dumped into a receiving vessel that has adequate venting capacity.

Most previous bottom venting systems have used automatic valves *(1, 2)*. Usually, such valves can be opened upon operator intervention by hitting a reactor dump switch or by safety interlocks that sense a high temperature or a high pressure in the protected vessel. A dump valve can be augmented by injecting inert gas into the top of vessel to help drive out the liquid.

This article focuses on the use of gas pressure generated by the early portion of a runaway reaction to open a passive pressure relief device. Although this setup may not open as quickly as the automatic valve actuated by a safety interlock, it has the advantage that it should work with a higher level of reliability without the need for an external energy source. The use of a dual system, employing both an instrumented dump system and a PBVR system in parallel should be considered when designing relief protection for energetic liquids.

Reactive fluids

Whereas PBVR has been comparatively rare, instrumented bottom dump systems have been widely used to protect reactors from runaway reactions. There are at least three reasons:

1. Instrumented dump systems can be actuated either by operator intervention or by a safety interlock that detects conditions that could lead to a runaway reaction. In contrast, a PBVR system depends on the pressure rise caused by gases evolved during the runaway reaction to open a passive pressure relief device. Thus, the instrumented dump system may be able to open sooner than the passive one.

2. For the PBVR system to function correctly, the vapor space in the vessel must be engineered to retain a sufficient quantity of the evolved reaction gases to force the liquid out of the protected vessel. Many reactors are designed to maintain constant pressure in their vapor space by use of an automatic control valve in an overhead vent line that vents gas when the pressure rises above a set point. The design engineer must be sure that the rate of gas evolution by the reaction will greatly exceed the maximum vent rate through the pressure control vent of the reactor if bottom venting is to work.

3. Properly engineered control valves in instrumented dump systems are less prone to leakage than relief valves and less prone to accidental opening than rupture disks.

Although there are few technical papers on PBVR systems, pressure relief experts can cite a number of examples of bottom venting in commercial practice. In the 1970s, a major U.S. chemical firm was using PBVR to vent runaway styrene polymerization reactions. The reactors operated above atmospheric pressure, but upon a high reactor pressure caused by a runaway polymerization, a rupture disk on the bottom of the reactor burst, allowing the unit to empty by gravity flow into a horizontal, cylindrical catch-tank. Large slots, parallel to the main axis of the tank, were on the top of the catch-tank to permit venting of gaseous byproducts from the polymerization reactions. An angular “rain hat” roof was aligned over the slots to keep rainwater out of the tank. The polystyrene remaining in the tank after the polymerization reactions were complete was very tough and difficult to remove. Therefore, the used catch-tank was disconnected and buried in a secure landfill. Then a new tank was installed.

Published evidence that bottom-venting systems were considered previously includes the SAFIRE computer code, which was developed under contract to AIChE as one product from the Design Institute for Emergency Relief Systems (DIERS). For example, see Fisher *et al. (3)*. The SAFIRE code, which was developed during the early 1980s, includes PBVR as a design option.

Two technical papers on PBVR were presented at the 1996 Process Plant Safety Symposium *(4, 5)*. Ref. 4 is only an abstract, and represents the first publication of this work.

Wakker and de Groot *(5)* of Akzo Nobel’s Central Research and Safety Depts. summarized extensive experimental work with unstable organic peroxides. They demonstrated the advantages of PBVR by experiment with a number of compounds. They also provided a number of practical suggestions for the application of bottom venting to full-scale systems. Their paper is must reading for anyone working with organic peroxides, or with a strong interest in PBVR.

A recent book *(6)* on chemical reaction relief outlines methods for the design of both bottom and top venting relief systems for reactive liquids.

Nonreactive fluids

In a related area of chemical engineering practice, blowdown systems have been used for decades for emergency depressurization of vessels containing oil and gas. Although chemical reactions are usually insignificant in blowdown of vessels containing hydrocarbon fluids, the choice of top vs. bottom venting is important. Mahgerefteh *et al. (7)* showed that bottom-venting depressurization of vessels containing hydrocarbon liquids reduced liquid inventories much more quickly than top venting. This observation applied to venting of both light and heavy hydrocarbon liquids. However, top venting depressurized vessels containing heavy hydrocarbons more quickly than bottom venting. For vessels containing light hydrocarbons, bottom venting gave superior depressurization, as well as quicker removal of inventory. Naturally, these observations depend on the size of the depressurization valves and piping that are mounted either on the top or on the bottom of the vessel.

Montgomery *(8)* developed a simplified model of the temperatures of both the vessel and the expanding gas within it during depressurization. Cooling during depressurization may be sufficient to require more expensive materials of construction that do not embrittle at the low temperatures achieved during this process. Montgomery found that the temperature of an expanding gas may be much lower than that of the vessel containing the gas, depending on heat-transfer rates. For vessels that are not insulated, either bottom venting (of vessels containing volatile liquids), or slower depressurization can keep vessel wall-temperatures from reaching the embrittlement range.

Haque *et al. (9)* formulated a sophisticated computer model for either top or bottom blowdown of vessels containing as many as three fluid phases (liquid water, liquid hydrocarbon, and wet-gaseous hydrocarbon). Their model can simulate a variety of complex phenomena, including cooling due to gas expansion, condensation of gas due to cooling, vaporization of liquids due to depressurization, formation of gas hydrates, heat and mass transfer between phases, and heat transfer to the vessel. Haque *et al. (10)* then verified the model for light hydrocarbons. They also demonstrated the advantages of bottom venting for rapid deinventory of contained liquids.

Advantages of bottom venting

Great care is essential when designing emergency relief systems for vessels that contain reactive liquids. This is because the energy released upon a spontaneous chemical reaction by these liquids can be large enough to cause serious damage if not safely relieved. For example, it is not unusual for the heat of reaction to be of the order of thousands of Btus per pound of reactive liquid. Many organic liquids have heat capacities of about 0.5 Btu/lb of liquid. Thus, adiabatic temperature rises could be several thousand degrees in the absence of vaporization. Because a 10°C temperature rise roughly doubles the reaction rate of many chemical reactions, even a 200°C rise can increase reaction rate by more than a million-fold. It is easy to see how a runaway reaction or self-accelerating decomposition (SAD) can occur, as heat released by the reaction accelerates it by increasing the temperature.

In practice, such extreme temperature rises are rarely achieved with reactive organic liquids of low to intermediate molecular weight. Instead, the thermal energy goes into vaporizing the liquid and raising the temperature of the vapor formed. In a pressure vessel with an inadequate pressure relief system, this will lead to a rapid increase in temperature and pressure, possibly followed by a catastrophic event.

Bottom-venting pressure relief systems offer the following advantages for vessels containing reactive liquids:

- Bottom venting is inherently safer, because liquid is removed from the process vessel quickly, thereby reducing conversions, temperatures, and reaction rates.
- The lower maximum temperatures achieved with bottom-venting systems may avoid the onset of hazardous secondary decomposition reactions that occur for a number of reactive chemicals. For example, chloroprene undergoes a ventable exothermic runaway polymerization at lower temperatures. At higher temperatures, this substance decomposes so rapidly that the reaction mixture is unventable.
- Bottom venting permits transfer of the reactive liquid from a process vessel into a quench vessel. The quench vessel can stop or retard a runaway reaction in several ways:
  1. If the reaction is tempered *(i.e.,* one or more of the principal components of the mixture is a volatile liquid that will boil and, thereby, keep the temperature of the mixture nearly constant), and if the relief pressure in the vessel is significantly higher than atmospheric, then dropping the reacting mixture into a tank that is open to atmospheric pressure will drop the temperature of the mixture, slowing or stopping the reaction.
  2. The quench tank receiving the reactor dump can contain a reaction-stopping compound as well as a mixing mechanism.

3. The tank can hold a significant inventory of water — enough to absorb the heat of reaction of the reactive mixture (as latent heat of vaporization of the water plus sensible heat).

- The bottom-venting relief system is often smaller and less expensive.
- For polymerizing systems, cleanup of the process vessels and piping is easier if the reactive process fluid is removed before much polymerization has occurred.
- For polymerizing systems, or for reactive systems that form other solids, bottom venting systems may be safer by virtue of being less likely to plug. This is because bottom venting usually removes the reactive fluid at much lower conversions than the top venting system.
- Reactive liquid can be transferred from an expensive vessel designed for manufacturing into an inexpensive one for quenching, mitigation, or venting of the runaway reaction, as well as for ease of cleaning.
- Bottom-venting pressure relief systems can be designed to operate passively, like top-venting ones. Passive venting systems obviate the need for an external energy source to open a valve.
- By mounting the pressure relief device on top of a dip tube into the process vessel, a bottom venting pressure relief device can be just as accessible for maintenance as a conventional top-mounted, top-venting relief device.

When to consider bottom venting

Bottom venting should be considered when any of the following conditions apply:

- When the contained liquid can undergo an unventable decomposition reaction.
- When the liquid can undergo an exothermic runaway reaction that requires an impracticably large top-venting pressure-relief system.
- When the liquid undergoes a runaway reaction that produces products, such as tough polymers, that are hard to remove from the process vessel, piping, and other process equipment.
- When the liquid is highly toxic itself, or the runaway reaction produces one or more products with high toxicity, thereby increasing the potential hazards associated with loss of containment.
- When the unreacted liquid is sufficiently valuable to make recovery from a partially reacted and quenched mixture attractive.

Elements in a bottom-venting relief system

A PBVR system may contain the following elements *(11)*:

- Inlet nozzle, dip pipe, or other inlet piping connecting the liquid in the vessel to the relief device;
- Pressure relief device;
- Outlet piping to a deck or disposal system;
- Vapor/liquid separator or quench tank; and
- Passive scrubber, burn pit, active scrubber, flare, or other disposal system.

In the PBVR system, the pressure relief device opens when the pressure inside the vessel reaches either the set pressure (relief valve or rupture pin) or the burst pressure (rupture disk) of the device. No external source of energy is required.

A PBVR system may include a pressure-control system for the vapor space of the protected vessel. For example, in a stirred tank reactor that operates with a liquid level about 60–80% full, the typical pressure-control system will let gas either out of or into the vapor space. When the reactor is being filled, one control valve in a vapor vent line will open when the pressure begins to rise, keeping the pressure nearly constant. Similarly, when liquid is being withdrawn, another control valve in an inert gas line will open to maintain the pressure nearly constant again. The flow of inert gas keeps up a positive pressure in the vapor space of the vessel and prevents air from entering through any leaks. Exclusion of air is recommended whenever the process liquid is flammable.

When designing a PBVR system for a vessel that also has a pressure control system, the design engineer should recognize that the pressure control valve in the overhead vent line would normally go full-open when the pressure inside the vessel approaches the relief value. The engineer should, therefore, allow for a slower emptying of the vessel by the PBVR system, because there will not be as much gas available to drive the liquid out of the vessel.

However, the engineer should also design the PBVR system to safely relieve the vessel if the control valve in the overhead vent line is closed because the control system is either offline or malfunctioning. In other words, because the control valve in the overhead vent line requires an external source of energy to open or close, its reliability may not be as high during an emergency. The designer should, therefore, be sure that the PBVR system would provide safe pressure relief, regardless of whether the control valve in the overhead vent line is open or closed.

For particularly reactive fluids, consider providing both instrumented dump and PBVR systems. This combination provides both high reliability and quick transfer of reactive liquid from the protected vessel into the appropriate receiving vessel.

Design guidelines

Here is a step-by-step procedure:

Step 1: Review the potential reasons for considering bottom venting.

Examine the vessel and the fluid it contains from the perspectives given here. In particular, review the sections on the advantages of bottom venting for reactive liquids and on when to consider bottom venting. If bottom venting does not appear to offer advantages for the vessel in question, stop considering it.

Step 2: Develop a preliminary qualitative design of bottom-venting system.

If you are new to pressure relief system engineering, additional reading is advisable, such as the API Guidelines *(12, 13, 14),* a CCPS monograph *(15),* and the book on reactive relief *(6).* Then, make the following choices:

a. Where will the bottom-venting relief device be located? On a nozzle on the bottom of the vessel? On top of a dip tube that reaches to near the bottom of the vessel? Or elsewhere?

b. What type of relief device will be used? Pressure relief valve? Rupture disk? Rupture pin? Rupture disk beneath a relief valve?

c. Where will the outlet piping discharge from the relief device? To the deck? To a relief effluent-handling system?

d. Is two-phase, vapor/liquid relief likely to occur? If so, a vapor/liquid separator will probably be needed *(16).*

e. Will a quench liquid be needed to stop the runaway reaction, or can the reaction be allowed to run its course *(17, 18, 19*)? If a quench liquid needs to be mixed with the vented liquid, should an active quench liquid-injection system be used, or will it suffice to use passive mixing in the quench tank?

f. If flammable vapors are released adjacent to the protected vessel, are there ignition sources in the area? If the vented vapors are toxic or flammable, will they need treatment? If so, what is the best treatment system (active scrubber, passive scrubber, flare, thermal oxidizer, catalytic oxidizer, etc.)?

g. Would it be advisable to install an instrumented dump system in parallel with a PBVR system? Should the passive system be augmented by injecting inert gas early during the event? This gas would accelerate flow to the bottom dump before the pressure generated by the reacting, vaporizing liquid is high enough to open the passive device and drive liquid from the vessel.

Step 3: Develop a preliminary qualitative design of top-venting system.

Use a procedure analogous to that in Step 2 for the bottom-venting system.

Step 4: Compare the preliminary designs; if possible, make a choice.

Are there any special characteristics of the particular reactive liquid and protected vessel that make for a clear choice? For example: Are there major differences in the safety or exposure to vapors, residues, or contaminated equipment? Does the size and footprint of the relief venting and effluent treatment system conform to the available space?

If a choice is clear, go to Step 5. If not, go to Step 6.

Step 5: Develop a quantitative design of the selected venting system. Review the results to be sure that the chosen selection still appears to be the correct one. Go to Step 7.

Step 6: Develop quantitative process designs of both types of venting systems. Review the results and select the best pressure relief venting system. Go to Step 7.

Step 7: Complete detailed engineering design of the selected type of pressure relief venting system. Document this design. Solicit review of the design by a competent peer. Conduct an engineering safety review of the design. Revise the design as needed.

Step 8: Order appropriate relief device(s), inspect and test device(s), and then install the new pressure relief system. Do likewise for ancillary equipment, such as the relief effluent-treatment system.

Step 9: Inspect relief systems during the prestartup safety review to assure that designs are implemented and installed properly. Start up and run unit.

Design hints

1. For vessels that would normally have a vapor space above the reactive liquid, top venting can often be made to be vapor-only relief by selecting an appropriately low maximum liquid level in the vessel. This greatly decreases the cost of the pressure relief system. For nonfoamy liquids with a viscosity less than 100 cP, the maximum allowable liquid level for either reactive or external heating may be estimated using the DIERS disengagement criterion *(3, 15).*

2. When the relief system's controlling design scenario is external fire exposure to a process vessel that results in a runaway chemical reaction, consider measures such as NFPA-recommended water spray, NFPA-recommended drainage, and NFPA-recommended insulation to reduce the external heat input by fire. These steps reduce the size of the required relief system; they may also increase the allowable liquid level in the vessel. They also decrease the risk of a boiling liquid expanding vapor explosion (BLEVE) of the protected vessel.

3. Modeling of a runaway reaction requires a kinetic model that fits reliable measurements of the reaction kinetic data (such as concentration vs. time for every chemical species in the reaction, plus temperature and pressure vs. time). The kinetic model should be based on data that cover the range of composition, catalyst characteristics, temperature, and pressure that would occur with an actual relief event in the full-scale equipment.

4. Because runaway reactions lead to significant temperature increases, pressure relief events caused by them may occur over a wide range of temperatures. Therefore, model the temperature dependence of liquid-phase properties such as density, heat capacity, heat of vaporization, and viscosity, as well as the temperature and pressure dependence of vapor-phase properties such as density and heat capacity.

5. If design conditions should assure all-vapor venting for the top venting design cases, then the appropriate nozzle flow equations from the API guidelines can be used to predict the venting rate through a given relief device orifice *(12, 14).*

6. There are two main choices for bottom venting: (a) venting through a nozzle on the bottom of the vessel; or (b) venting flowing upward through a dip tube that penetrates the top of the vessel. These two main choices may lead to very different flow phenomena in the nozzles, resulting in different nozzle flow models. For example, if a rupture disk is to be mounted on a bottom nozzle of the vessel, then hydrostatic pressure will cause the liquid at the nozzle entrance to be subcooled during most of the relief event. This may be true even if the liquid at the top of the liquid surface in the vessel is boiling. Therefore, the bottom-mounted relief device may be represented to a first approximation by using the nozzle flow model for subcooled liquids.

7. Conversely, a rupture disk may be mounted at the top of a dip pipe that penetrates the top head of the protected vessel, with the other end of the pipe submerged to near the bottom of the protected vessel. Then, although the liquid entering the bottom end of the dip pipe will be subcooled, by the time it has reached the rupture disk at the top of the pipe, the hydrostatic head will be much less. The liquid at the rupture disk will be flashing if the liquid in the top of the protected vessel is at its bubble point. This means that, for most systems, the rupture disk mounted on the bottom nozzle of a vessel can be significantly smaller in diameter than the dip pipe and corresponding rupture disk.

8. Plugging of the emergency relief system can be caused by the gradual accumulation of polymers or other solids. Plugging must be prevented. One way to achieve this is to purge the inlet to the relief system with a solids-free fluid, such as an inert gas, the process solvent, the process monomer, or another acceptable liquid.

Top vs. bottom venting: Examples

Reactive liquids are found in virtually all types of process equipment. Perhaps, the two most common types that contain significant inventories of process fluid are the cylindrical vessel or tank, and the heat exchanger. The advantages of bottom venting are illustrated below for these two widely used vessels. The two cases were compared using a computer program developed by the authors. The program determined the minimum size of relief-valve orifices required for both bottom and top venting during the same relief scenario. The program is primarily applied to reactive systems that are either gassy or hybrid, as these are often attractive candidates for bottom venting.

The program sequentially solves a series of first-order differential equations with time as the independent variable. Normally, the program begins with the system at normal operating temperature, pressure, and fill volume. Then, either a fire begins (usually with immediate, full heat flux) or the reaction(s) start when some initiating event occurs. Generally, the program begins with a relief valve containing a "D" orifice in vapor venting. When it determines the smallest orifice for vapor venting and prints these results, it returns to a "D" orifice to begin liquid venting. Eventually, it finds the smallest orifice for liquid venting, prints these results, and then stops.

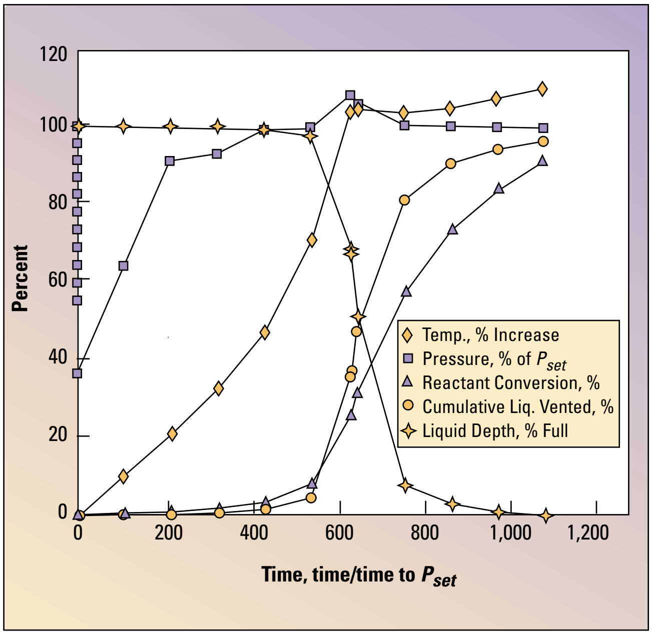
Heat exchanger

Consider a vertical one-pass heat exchanger exposed to an external fire. Its contents undergo a hybrid reaction. The exchanger is 12 in. dia. The reactive process liquid is inside the tubes and heads. The liquid is essentially 100% Reactant A, which reacts to form noncondensable Gas G and relatively nonvolatile Liquid B. Reaction kinetics are first-order in Reactant A, and are well-fit by an Arrhenius relation based on experimental data. The normal operating conditions are 55 psig and 150°C, and the relief valve is set to open at 100 psig.

The relief scenario modeled assumes that the cooler is blocked in at normal operating conditions, that a fire starts that boils away the shell's cooling water, and that the fire transmits heat by radiation through the shell to the tubes, in addition to heat transmitted directly through the heads. The vent rate is low enough such that the top head provides sufficient disengaging space for all-vapor venting once the liquid level drops in the top head. Since the exchanger is initially full of liquid, it is assumed that thermal expansion and reaction in the tubes during the shell boilout have removed the liquid above the top head. Consequently, only single-phase vapor venting is modeled.

Conventional top venting:

The relief valve containing an "N" orifice is mounted on the top head.



■ Figure 1. Conventional top venting: vertical one-pass heat exchanger.

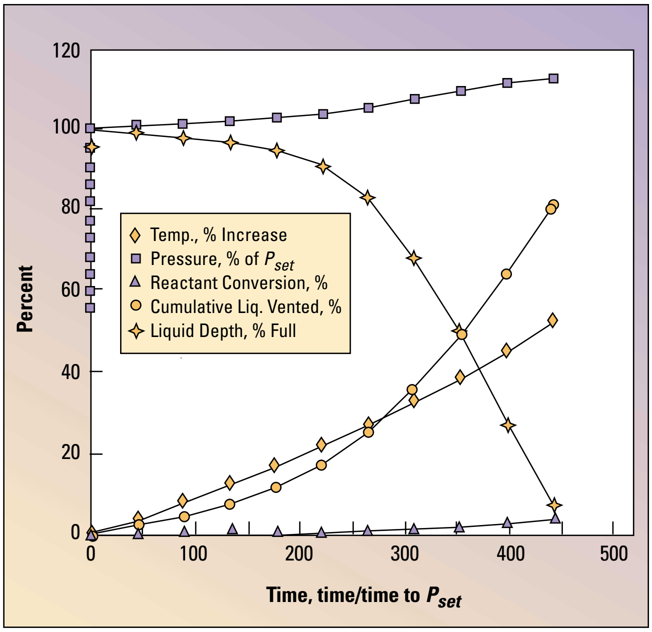
Figure 1 shows dimensionless values of key variables resulting from the numerical FORTRAN simulation. The time abscissa is in the time since heating begins (instantaneous full-fire heat flux is assumed) divided by the time required to reach the set pressure. The ordinate is in terms of percent for five variables: (1) temperature (measured as percent increase above the normal operating temperature); (2) pressure (percent of the relief valve's set pressure); (3) Reactant A conversion (percent conversion of the liquid remaining in the cooler, not the conversion of the initial liquid, since some A is vented with the vapor); (4) cumulative Liquid A vented (percent of that initially in cooler); and (5) liquid depth (percent full).

Because the cooler is nearly full of liquid, the set pressure is reached in just less than 0.5 s. The relief valve quickly pops open to vent a small amount of vapor and then quickly recloses, since the pressure falls rapidly. The simulation closes the relief valve when the blowdown pressure is reached, and then reopens it when the set pressure is again achieved. It takes nearly 200 dimensionless time units before a total of 1 lb of vapor has been vaporized (out of the 826 lb of liquid initially blocked in). During this time, the temperature rises about 21% and the reactant conversion is about 0.5%. At this point, the rate of heat input due to the reaction is 13% of the total heat input. The pressure rapidly rises to the set pressure and falls back many times during this period. The pressure shown on the graph is actually the low-point pressure reached after the valve recloses. This pressure curve steadily rises as the vapor volume in the cooler increases. Up to about 400 dimensionless time units, there is very little reactant conversion or drop in liquid level.

The peak pressure and the peak relief rate (46,000 lb/h) are achieved at 630 dimensionless time units, or just less than 5 min. At this point, the liquid level is about 67% of full, the conversion is 26% in the remaining liquid, and 36% of the original liquid has been vented. The percentages of liquid level and venting do not sum to 100%, because the liquid continues to swell as the temperature rises. At this point, only about 15% of the total heat input comes from the heat of reaction, even though the temperature has doubled to over 300°C. The simulation model accounts for the fire heat-input dropping as the liquid-wetted area falls.

The simulation actually began with the smallest "D" orifice relief valve, but when the maximum pressure exceeded the 21% overpressure allowable for a fire scenario, the next larger orifice was tried. Eventually, the "N" orifice was the first for which the maximum allowable overpressure in the vessel was not exceeded during the simulation.

The simulation stops at about 1,075 dimensionless time units, or about 8.4 min, when the liquid level falls to zero. There is still about 4% of the initial liquid left in the piping; however, this endpoint is selected for comparison to the bottom venting case. At this point, the temperature has continued to rise to 314°C and the conversion exceeds 91%. Even at this high conversion, the reaction heat input has risen to only 17% of the total. The relief valve continues its opening/closing cycle, since the vent rate is insufficient to keep the pressure continuously above the blowdown pressure.



■ Figure 2. Bottom venting: vertical one-pass heat exchanger.

Bottom venting:

A liquid-trim relief valve containing an "F" orifice is mounted on the bottom head.

Figure 2 shows dimensionless values of key variables resulting from the numerical FORTRAN simulation. Variables are defined in the figure.

The simulation proceeds identically with the top-venting scenario until the relief valve first opens. From this point on, there is a dramatic difference. The valve does not continually pop open and close, as it did for top venting. At low overpressures, it is only slightly open. This is because a liquid-trim valve's relief flow is proportional to the overpressure. Although the pressure does drop below the blowdown pressure and close the valve, the pressure swings are much smaller, even for systems like this exchanger that have small vapor volumes. The pressure in the cooler's vapor space remains relatively constant over short periods. Over longer periods, it slowly increases until all the liquid has vented.

At a dimensionless time of 200, 17% of the liquid has already been vented. The temperature has risen 22% and the conversion is about 0.5%; 13% of the total heat input rate is from the exothermic reaction heat.

As in the top-venting case, the simulation stops when the liquid level falls to zero, but, in this case, only 440 dimensionless time units were required, or 3.4 min. The temperature has risen only 53% to 230°C, and the reaction conversion is only 3.8%; 49% of the total heat input is from the reaction heat, because the conversion is so low, even though the temperature is also low. The pressure is now at its peak of 13% above the set pressure, but below the allowable 21% overpressure. At this point, vapor begins to pass through the valve, but this portion of the event is not currently simulated or shown. The results from the two simulations are summarized in Table 1 to simplify comparison.

Table 1. Process (tube-side) relief for heat exchanger.

94 gal of process fluid initially; set pressure of 100 psig

Variable	**Top Vent**	**Bottom Vent**
Time to Empty, min	8.4	3.5
Relief Orifice Area, in.^{2}	4.34	0.307
Maximum Process Temperature, °C	314	230
Reaction Conversion, (%) at Empty	91.2	3.8

Stirred batch reactor

The unit is exposed to an external fire and its contents undergo a hybrid reaction. It holds approximately 1,500 gal including the heads, and is mechanically agitated. The maximum allowable liquid level (to avoid two-phase, vapor/liquid relief) is 74% full. The reactive liquid initially contains essentially 14% catalyst and 86% Reactant A, which reacts to form noncondensable Gas G and relatively nonvolatile Liquid B. Reaction kinetics are first-order in Reactant A, and are well-fit by an Arrhenius relation, based on experimental data. The normal operating pressure is just over atmospheric with an inert-gas pad, and the operating temperature is 105°C. The relief valve is set to open at 30 psig.

The relief scenario modeled assumes that the reactor is blocked in at normal operating conditions, and that a fire starts at time zero with full heat input.

Conventional top venting:

The relief valve containing an "L" orifice is mounted on the top head. Vapor-only flow occurs when the reactor is below 80% full; thus, 74% full is the maximum allowable fill level to account for liquid swell.

Figure 3 shows dimensionless values of key variables resulting from the numerical FORTRAN simulation. Variables are defined just as in the heat exchanger example above.

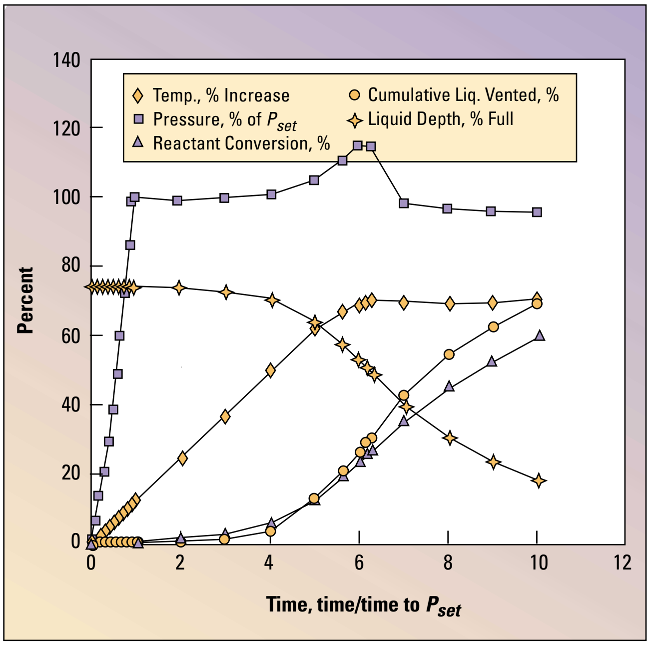
Because the reactor has a large initial vapor volume, it takes almost 6 min to reach the set pressure. The relief valve quickly pops open to vent a small amount of vapor and then quickly recloses, since the pressure falls a few 10ths of a psi below the blowdown pressure. The simulation closes the relief valve when the blowdown pressure is reached, and then reopens it when the set pressure is achieved. It takes about 2.0 dimensionless time units before a total of 25 lb of vapor has been vaporized (out of the 7,750 lb of liquid initially blocked in). During this time, the temperature rises about 24% and the reactant conversion is about 0.8%. The heating rate due to the reaction is now 9% of the total heat input. The pressure rises to the set pressure and falls back many times during this period.

The pressure curve holds nearly constant at the set pressure up to 4.0 dimensionless time units, when 4% of the liquid has been vaporized. At this point, the temperature has risen 50%, and there has been a 5.6% conversion.

The peak pressure 14.4% above the set pressure and the peak relief rate (12,400 lb/h) are achieved at 6.2 dimensionless time units, or at about 37 min. At this point, the liquid level is about 50% of full, the conversion is 25% in this remaining liquid, and 29% of the original liquid has been vented. About 39% of the total heat input comes from the heat of reaction, as the temperature has increased by 69% to 178°C. The simulation model accounts for the fire heat input dropping as the liquid-wetted area falls.

The simulation actually began with the smallest "D" orifice relief valve, but when the maximum pressure exceeded the 21% overpressure allowable for a fire scenario, the next larger orifice was tried. Eventually, the "L" orifice was the first one for which the maximum overpressure was not exceeded during the simulation.

The simulation arbitrarily stops after 1 h has elapsed, or about 10.1 dimensionless time units. At this point, the re-



■ Figure 3. Conventional top venting: stirred batch reactor.

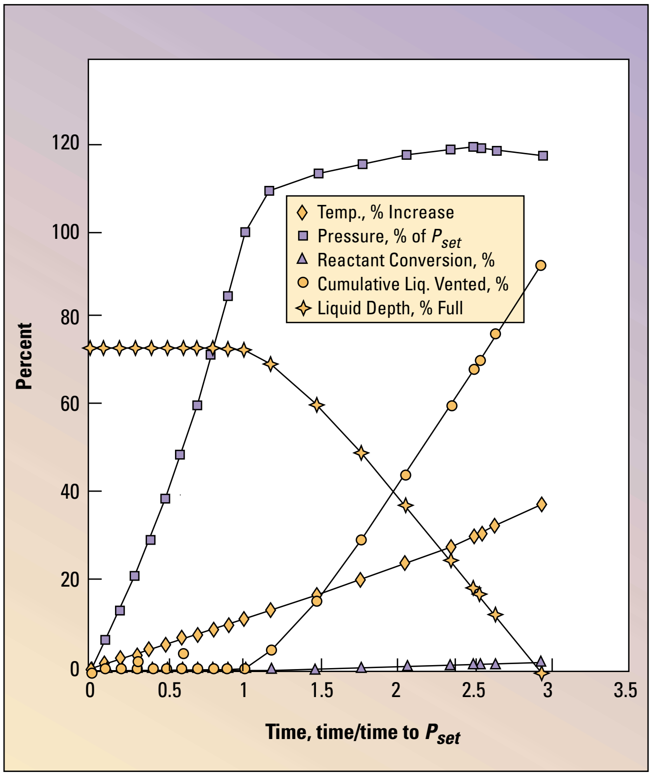


Figure 4. Bottom venting: stirred batch reactor.

lief valve is again cycling open/closed, as there is not a sufficient rate of vapor generation to keep it open. The liquid level has fallen to about 18% full, and 70% of the initial liquid has been vaporized and vented. The temperature has continued to remain nearly constant near its peak value of 178°C, and the conversion is about 60%. At this conversion, the reaction heat input has risen to 47% of the total. The relief valve continues its opening/closing cycle, since the vapor generation rate is insufficient to keep the pressure continuously above the blowdown pressure.

Although not followed by the model, venting would continue at progressively slower relief valve operating frequencies until either the liquid level dropped to zero or the reaction conversion reached 100%.

Bottom venting:

The liquid-trim relief valve containing an "H" orifice is mounted on the bottom head. An alternative location for the venting system is on the top head with a dip tube extending to the vessel's bottom.

Figure 4 shows dimensionless values of key variables resulting from the numerical FORTRAN simulation. Variables are defined as in all the other cases.

The simulation proceeds identically with the top-venting scenario until the relief valve first opens at a dimensionless time of 1.0. From this point on, there is a dramatic difference. The valve does not continually pop open and reclose as it did for top venting. It stays open continuously. At low overpressures, it is only slightly open. This is because a liquid-trim valve's relief flow is proportional to the overpressure. Because of the large vapor volume (compared to the heat exchanger's small vapor volume), the pressure in the reactor's vapor space remains relatively constant over short periods.

Table 2. Process relief for stirred batch reactor.

1,300 gal reactor; 960 gal fill volume; set pressure of 30 psig

Variable	**Top Vent**	**Bottom Vent**
Percent Empty	75%	100% (Empty)
Time, min	60	17.5
Orifice Area, in.^{2}	2.853	0.785
Maximum Reactor Temperature, °C	179	145
Reaction Conversion, %	59.8	2.2

The maximum pressure occurs at 19.3% over the set pressure (the allowable overpressure is 21% for the fire scenario) at a dimensionless time of 2.5, or just over 15 min. At this point, 71% of the initial liquid has been vented and the liquid level is at 17%. The temperature has risen 31% to 138°C. There has only been 1.4% reactant conversion, and the reaction heat input is only 12% of the total.

The simulation stops when the liquid level falls to zero, but in this case only 2.9 dimensionless time units were required, or 17.5 min. The temperature has risen only 38% to 145°C, and the reaction conversion is only 2.2%. Only 10% of the total heat input rate is from the reaction, because the remaining liquid is so low, even though the conversion is also low. The pressure has now dropped to 17.6% above the set pressure.

At this point, 93% of the initial liquid has been vented, and the remainder is in the piping. Now vapor begins to pass through the valve, but this portion of the event is not currently simulated or shown. Table 2 compares key results from the top and bottom venting cases.

To sum up

Bottom venting offers many advantages for pressure relief of reactive fluids. Passive bottom venting can be used to increase the reliability of instrumented emergency dump systems or, independently, as an improvement over conventional top-venting pressure relief systems.

In the examples given here, relief orifice areas for bottom venting were much smaller than those required for conventional top venting. Peak reaction temperatures were much lower with bottom venting, leading to significant decreases in reaction rates and conversions when compared to top venting systems. The dramatically lower reaction rates and the ease of quick external quenching of the reactive fluids make bottom venting inherently safer than top venting for many reactive fluids.

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