Rigorously Size Relief Valves for Supercritical Fluids

Ryan Ouderkirk,
Fluor Corp.

Previously published methods can be tricky to apply, and may lead to improperly sized valves. Here is a stepwise, detailed method that more-accurately determines the orifice area.

Supercritical fluids exhibit characteristics typical of both liquids and vapors. Transport properties, such as viscosity and diffusion rate, are closer to those of typical vapors, while solvent strength resembles that of typical liquids. Further, the properties can be strong functions of pressure and temperature, allowing the solvent strength to be easily manipulated. This led to the use of supercritical fluids in industrial processes such as extraction of caffeine from coffee with carbon dioxide, and the Residuum Oil Supercritical Extraction (ROSE) process with either butane or pentane *(1)*. However, these same deviations from both ideal gas and incompressible fluid behavior present distinct challenges for relief valve sizing.

Here is a rigorous procedure to calculate the relief rate and size the relief valve for supercritical fluids. The relief rate is modeled over time for a blocked-in vessel using small increments of temperature. The relief valve is sized by modeling mass flux through an isentropic orifice up to the limit of choked flow. An *n*-butane fire case will illustrate the procedure using Lee-Kesler properties *(2)*. The method is suited for other heat-input cases, as well as other property-determination methods.

Many relief problems are simplified significantly by assuming incompressible-fluid or ideal-gas behavior. A fluid at supercritical conditions can be quite compressible, and its physical properties may deviate appreciably from ideal-gas behavior. Relief venting of supercritical fluids has been studied previously, resulting in guidelines for calculating the relief rate *(3, 4)* and the relief-valve orifice area *(5, 6, 7)*. However, if one is not careful in reading these guidelines, he or she may size the relief valve based on ideal-gas simplifications or merely for the maximum mass relief-rate. The reader can inadvertently use the vapor or liquid sizing-equations (for an ideal or compressible gas), for example. Also, Ref. 4 tells the reader how to find the maximum relief rate, as opposed to the maximum orifice area. The maximum required orifice area may not occur at the maximum mass relief rate or the maximum volumetric relief-rate (Figure 1).

Here is a step-by-step procedure to rigorously size the relief valve for supercritical fluids. In presenting

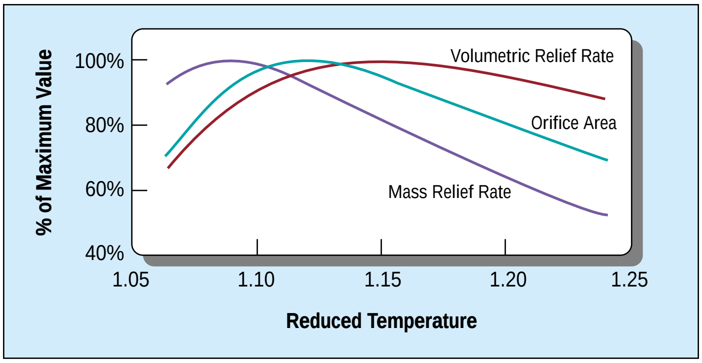

Figure 1. The maximum required orifice area may not occur when expected during relief venting.

this method, we will start by discussing the fluid conditions leading to supercritical relief. Then, the method will be presented in a simplified form, followed by a detailed step-by-step example to guide the user through the process, while highlighting potential problems with abnormal cases. Afterwards, we will cover the basis for the procedure: the required-relief-rate derivation and the relief-valve orifice-area derivation. Also, mention is made of several alternate procedures for sizing the orifice and of the potential for supercritical relief to turn into two-phase relief flow.

Consider a blocked-in vessel full of liquid with a vessel-relief pressure greater than the fluid's critical pressure. If heat is added by fire or other means, boiling cannot occur. Initially, heat causes the liquid to expand and the vessel to reach relief conditions. The relief valve can be sized for this condition with equations available in Ref. 5. If the heat continues, both the bulk temperature and the vapor pressure increase. The liquid may begin to flash in the discharge pipe and in the relief device. Once the vapor pressure exceeds the valve backpressure, more-sophisticated sizing methods are required to account for two-phase relief. Refer to API 520 Part I *(5)* for guidance on two-phase relief-valve sizing. Finally, if more heat is added, the fluid may pass through the critical temperature and the ensuing relief becomes supercritical. Such relief-valve sizing is detailed here.

The same general sequence of events may occur in a vessel partially full of liquid, except that the vapor space is removed initially. The vapor space may dissolve into the liquid as the solubility increases, or may pass through the relief device as the pressure increases. The pressure increases due to the increasing vapor pressure of the liquid and the compression of the vapor space by liquid expansion.

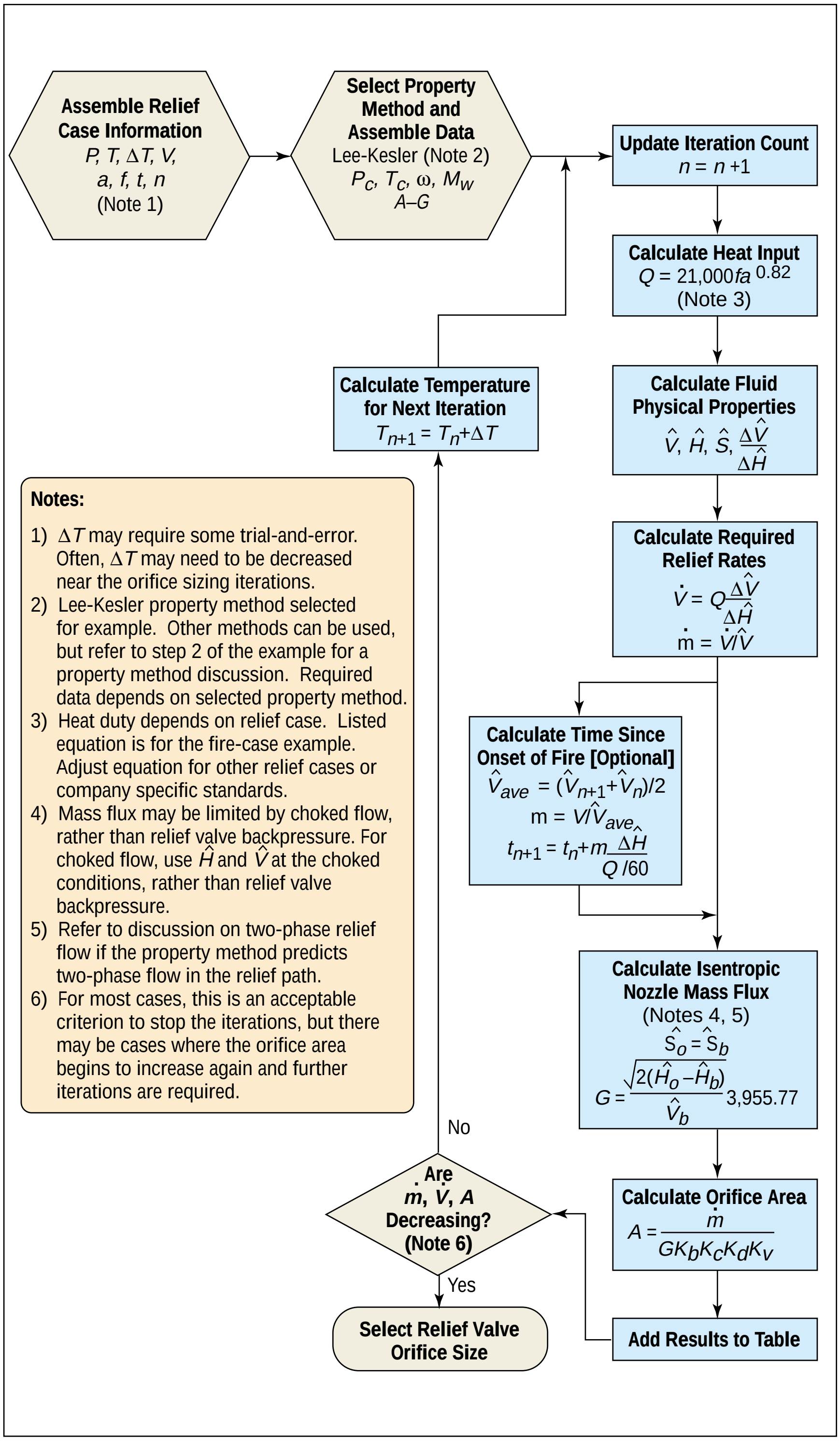

Figure 2. A simplified logic diagram for sizing relief valves for supercritical fluids.

Summary of method

The case considered here is heat from a fire or other means. The fluid does not boil, since the relief pressure is above the fluid's critical pressure. Without boiling, the temperature will continue to rise until the heat input is zero. Since supercritical fluid properties

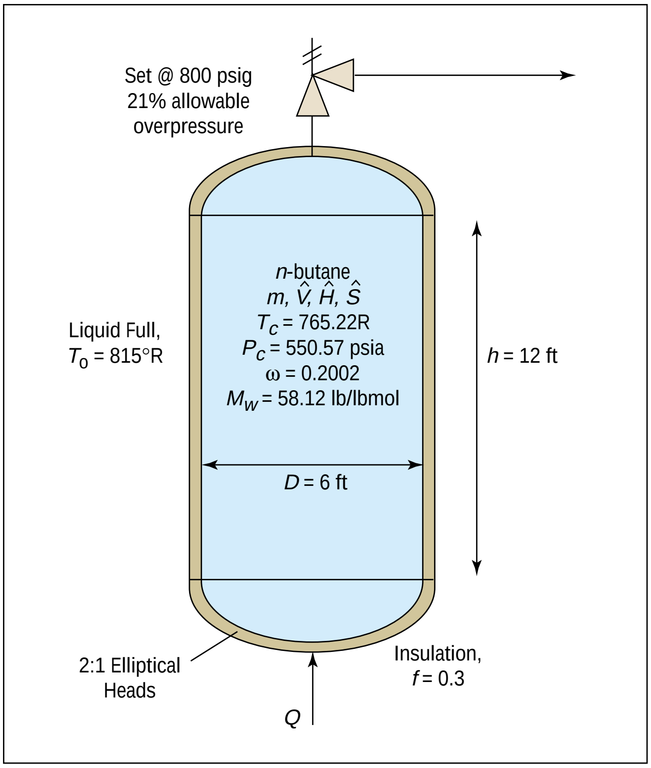

Figure 3. Fire-case example for *n*-butane.

can be strong functions of temperature and pressure, the vessel may require a dynamic model to account for the rising temperature and a potentially increasing relief rate and orifice area. This procedure embodies such a dynamic model for the relief device, and includes the sizing procedure from calculating the relief rate through sizing the orifice. The dynamic model is controlled by the increase in temperature of the vessel contents. For each temperature, the relief rate is first calculated based on the fluid physical properties and the heat input; then the relief valve is sized by assuming isentropic orifice flow (Figure 2).

Stepwise example

Consider a blocked-in vessel initially full of *n*-butane at the conditions shown in Figure 3. Relief is needed due to a fire of unknown duration.

Step 1: Assemble the relief case information:

$P, T, \Delta T, V, a, f, t, n.$

From Figure 3, the vessel is initially at 815°R. The relief-valve set-pressure is 800 psig with a 21% allowable overpressure for the fire case. In reality, the vessel pressure will vary during relief. First, the added heat is enough to cause the vessel to reach the relief-valve set-pressure. Then, the valve opens and partially empties the vessel. The valve may reseat and possibly chatter or flutter since it may be slightly oversized. The process repeats until the fire is extinguished. With a properly sized valve, the vessel never reaches the allowable overpressure of 21%. However, for simplification, assume that the vessel is initially at the allowable overpressure and remains so throughout the relief case. So, T = 815°R; $P = 1.21 \times 800 + 14.7 = 982.7$ psia.

A temperature change must be selected for the iteration. This requires trial-and-error. With decreasing increments, the relief rate and orifice area should converge to a solution. Often, a large change can be tried to broadly establish the range that leads to the maximum orifice area. Then, a smaller change can be used throughout that range to accurately find the maximum required orifice area. For the example, 2°R appears to be sufficient: Thus, ΔT = 2°R.

Next, calculate the vessel properties. Volume and surface area for different types of vessel heads can be estimated using Ref. 9. Guidelines for the environmental factor, *f*, are found in Ref. 3. To calculate the vessel volume, the wall thickness is ignored, as is the slight expansion caused by the increasing wall temperature. To find the wetted-surface area, assume that the vessel is completely engulfed in flames with all of its walls wetted by the supercritical fluid. The top head area is included in this calculation, but this may be conservative. Also, the vessel is assumed to be isolated from the piping system, so pipe surfaces are not included. The insulation is fireproof and an environmental factor of $f = 0.3$ is assumed.

$$V = \frac{\pi}{4} D^2 h + 2 \times \frac{\pi}{24} D^3 = 395.8\,\text{ft}^3 \qquad (1)$$

$$a = \pi\, Dh + 2 \times 1.084 D^2 = 304.23\ \text{ft}^2 \qquad (2)$$

Now, initialize the variables for time, t, and the number of iterations, n. $t = 0$ and $n = 0$.

Step 2: Select the property-estimation method and assemble the data:

P_c, T_c, ω, M_w, A–G.

n-butane is a nonpolar, single-component hydrocarbon, so the Lee-Kesler method *(2)* should suffice. Lee-Kesler, or a slightly modified version, is available in most commercial simulators. Since supercritical relief typically occurs in the region of highest uncertainty for most property-determination methods, the physical properties should be checked against laboratory data, if possible.

Discussing the proper selection of a method is beyond the scope of this article, but Lee-Kesler offers two major benefits. One is the integration of the thermal properties (enthalpy and entropy) with the other physical properties. Some methods require a separate determination for thermal properties. However, thermodynamic cohesiveness may not exist between the

Nomenclature

References denote sources of data.

a = fire case, total wetted surface area, ft^2
A = required relief-valve effective orifice-area, $in.^2$
A, B, C, D, E, F, G = ideal-gas thermal property coefficients *(8)*
D = vessel outside dia., ft
f = environmental factor from API 521 section 3.15 *(3)*
G = theoretical relief-valve mass-flux, $lb/h \cdot in.^2$
h = vessel tangent-to-tangent height, ft
H = relief- or vessel-fluid enthalpy, Btu
K_b = relief-valve capacity correction factor due to backpressure *(5)*
K_c = relief-valve combination correction factor for rupture disc *(5)*
K_d = relief-valve effective coefficient of discharge *(5)*
K_v = relief-valve viscosity correction factor *(5)*
m = relief- or vessel-fluid mass, lb
n = number of iterations
M_w = molecular weight, lb/lb-mol
Q = relief-case heat input, Btu/h
Q_{rev} = reversible heat input causing entropy to increase, Btu
P = pressure, psia
R = ideal gas constant, 10.73 psia ft^3/lb-mol·°R or 1.986 Btu/lb-mol·°R
S = relief- or vessel-fluid entropy, Btu/°R
t = time since onset of fire, min
T = temperature, °R
v = velocity of fluid through orifice, ft/s
V = Relief- or vessel-fluid volume, ft^3
z = fluid compressibility factor, dimensionless

Symbol
ω = fluid acentric factor, dimensionless

Subscripts
ave = average
b = at outlet of relief valve orifice
c = critical point
IG = ideal gas
r = reduced or residual
0 = initial value or at inlet of relief valve orifice

Superscripts
0, 1 = first- and second-residual property terms per Lee-Kesler *(2)*
^ = mass, /lb
• = time, /h

two methods. The second benefit is the integration of liquid and vapor properties into a single correlation. Some procedures use two distinct correlations for liquid and vapor properties, so the following caution should be observed:

Although there is no distinguishable transition from supercritical liquid to supercritical vapor, some methods must make a transition from the liquid to the vapor correlation. This may lead to a discontinuity in the physical property or in the change of the property with respect to temperature or pressure.

For this relief-valve-sizing method, the property method must be continuous for both a physical property and the change with respect to temperature and pressure.

For Lee-Kesler, the critical properties and ideal-gas thermal property coefficients are required and can be assembled from publications, such as Ref. 8. To calculate the residual properties with Lee-Kesler and the ideal-gas thermal properties, the following *n*-butane properties are assembled:.

P_c = 550.57 psia; T_c = 765.22°R; ω = 0.2002; M_W = 58.12 lb/lb-mol.

A = 7.228140; B = 0.099687; $C \times 10^4$ = 2.66548; $D \times 10^8$ = 5.4073; $E \times 10^{11}$ = –4.29269; $F \times 10^{15}$ = 6.69580; G = 0.345974.

Other pertinent information found in the "Data Book" *(8)* are the details of both the Lee-Kesler and the ideal-gas thermal-property methods, a useful discussion on critical properties, and recommendations for calculating critical properties of mixtures.

Step 3: Update the iteration count. For the first step, $n = n + 1 = 0 + 1 = 1$.

Step 4: Calculate the heat input, Q. For this fire case, the heat absorption rate for the vessel is calculated by assuming that Eq. 3 from API 521, Section 3.15.2 *(3)* represents the heat absorbed by a supercritical fluid with adequate drainage and prompt firefighting *(4)*:

$$Q = 21,000\, fa^{0.82} = 21,000 \times 0.3 \times 304.23^{0.82} = 684,800 \text{ Btu / h} \quad (3)$$

This equation can be modified for company-specific standards or other heat-input cases. Ref. 4 suggests that the heat absorbed by the fluid can more-accurately be modeled by subtracting out the heat absorbed by the vessel wall. For simplification, this has been ignored, even though the wall may act as a significant heat sink.

In this case, the heat duty is assumed to be constant throughout the relief case. However, for cases such as a blocked-in heater, the heat duty may vary with vessel temperature, and the duty may need to be recalculated for each iteration.

Step 5: Calculate the physical properties of the fluid: $\hat{V}, \hat{H}, \hat{S}, \Delta\hat{V}/\Delta\hat{H}$.

Any of the commercial simulators may significantly simplify these calculations. For this example, the Lee-Kesler property method was selected in Step 2. For more detailed information on Lee-Kesler see Ref. 2. The fluid is defined by the pressure from Step 1 and the temperature from either Step 1 for the initial case (n = 1) or the value calculated in Step 12 for all other cases. These example calculations apply to the initial case, T = 815°R.

If a simulator is used, it will complete most of the remaining calculations in this step. To find the Lee-Kesler

properties without a simulator, first compute the reduced pressure and temperature using the critical properties from Step 2:

$$P_r = \frac{P}{P_c} = \frac{982.7\,\text{psia}}{550.57\,\text{psia}} = 1.785 \quad (4)$$

$$T_r = \frac{T}{T_c} = \frac{815°\text{R}}{765.22°\text{R}} = 1.065 \quad (5)$$

Next, determine the appropriate residual properties based on reduced temperature, reduced pressure, and the acentric factor from Step 2.

$$\begin{aligned} z &= z^0 + \omega z^1 = 0.341304 + 0.2002 \times 0.016560 \\ &= 0.344619 \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{\hat{H}_r}{RT_c} &= \frac{\hat{H}_r{}^0}{RT_c} + \omega \frac{\hat{H}_r{}^1}{RT_c} = 3.14750 + 0.2002 \times 1.72587 \\ &= 3.49302 \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{\hat{S}_r}{R} &= \frac{\hat{S}_r{}^0}{R} + \omega \frac{\hat{S}_r{}^1}{R} + \ln\left(\frac{P}{14.7}\right) = 2.3214 + 0.2002 \times 1.6658 \\ &+ \ln\left(\frac{982.7}{14.7}\right) = 6.8573 \end{aligned} \quad (8)$$

To calculate the residual properties, Lee-Kesler provides both tables and figures for hand calculations and equations for a computer model. To find the relief rates, a small temperature change is used to estimate the changes in the physical properties. Since these changes can be small, a considerable number of digits need to be carried through the calculations; a hand calculation is not recommended. A spreadsheet model was setup with macros to solve both the Lee-Kesler properties and the relief-valve orifice area. If a hand calculation is necessary, the enthalpy and specific-volume changes found later in this step should probably have a minimum of three significant digits. This means that more digits should be carried through the procedure when using smaller temperature increments.

Now, find the ideal-gas thermal properties for the enthalpy and entropy based on Ref. 8 and the coefficients from Step 2: For the T = 815°R initial case:

$$\begin{aligned} \hat{H}_{IG} &= A + BT + CT^2 + DT^3 + ET^4 + FT^5 \\ &= 278.2615\ \text{Btu/lb} \end{aligned} \quad (9)$$

$$\begin{aligned} \hat{S}_{IG} &= B\ln(T) + 2CT + \frac{3}{2}DT^2 + \frac{4}{3}ET^3 + \frac{5}{4}FT^4 + G \\ &= 1.47525\ \text{Btu/lb}\cdot°\text{R} \end{aligned} \quad (10)$$

Calculate the actual specific volume, enthalpy and entropy. The molecular weight is taken from Step 2:

$$\begin{aligned} \hat{V} &= \frac{zRT}{PM_w} = \\ &\frac{(0.344619)(10.73\ \text{psia} \times \text{ft}^3/\text{lbmol}\bullet°\text{R})(815°\text{R})}{(982.7\ \text{psia})(58.12\ \text{lb/lbmol})} \\ &= 0.0527655\,\text{ft}^3/\text{lb} \end{aligned} \quad (11)$$

$$\hat{H} = \hat{H}_{IG} - \left(\frac{\hat{H}_r}{RT_c}\right)\frac{RT_c}{M_w} \quad (12)$$

$$\begin{aligned} \hat{H} &= 278.2615\,\text{Btu/lb} \\ &- \frac{(3.49302)(1.986\,\text{Btu/lbmol-°R})(765.22°\text{R})}{58.12\ \text{lb/lbmol}} \\ &= 186.926\,\text{Btu/lb} \end{aligned} \quad (13)$$

$$\begin{aligned} \hat{S} &= \hat{S}_{IG} - \left(\frac{\hat{S}_r}{R}\right)\frac{R}{M_w} = \frac{1.47525\,\text{Btu}}{\text{lb}\cdot°\text{R}} \\ &- \frac{(6.8573)(1.986\,\text{Btu/lbmol}\cdot°\text{R})}{58.12\ \text{lb/lbmol}} = \frac{1.2409\,\text{Btu}}{\text{lb}\cdot°\text{R}} \end{aligned} \quad (14)$$

Finally, determine the volumetric expansion term by calculating the specific volume and enthalpy at the relief pressure, and after the temperature increase selected in Step 1 (2°R), *i.e.*, 982.7 psia and 817°R for this first iteration. The expansion term can then be calculated from the change in properties, but may need to be found outside of a simulator if using one:

$$\begin{aligned} &\hat{V} = 0.0536716\ \text{ft}^3/\text{lb};\ \hat{H} = 189.196\ \text{Btu/lb} \\ &\frac{\Delta\hat{V}}{\Delta\hat{H}} = \frac{0.0536716\ \text{ft}^3/\text{lb} - 0.0527655\ \text{ft}^3/\text{lb}}{189.196\ \text{Btu/lb} - 186.926\ \text{Btu/lb}} \\ &= 0.000399163\ \text{ft}^3/\text{Btu} \end{aligned} \quad (15)$$

Step 6: Calculate the required relief rates: $\hat{V}, \hat{m}$.

The derivations of the relief-rate formulas are presented later on in this article. The required relief rates for the first iteration are found using the heat input and physical properties from Steps 4 and 5:

$$\dot{V} = Q\frac{\Delta\hat{V}}{\Delta\hat{H}} = 684,800 \text{ Btu / h} \times 0.000399163 \text{ ft}^3 \text{ / Btu}$$
$$= 273.3 \text{ ft}^3 \text{ / h} \quad (16)$$

$$\dot{m} = \dot{V} / \hat{V} = \frac{273.3 \text{ ft}^3}{\text{h}} / \frac{0.0527655 \text{ ft}^3}{\text{lb}} = 5,180 \text{ lb / h} \quad (17)$$

Step 7: Calculate the time elapsed since the onset of the fire, t (this step is optional).

This time interval is not needed to find the required orifice area. However, the computation may prove useful for fires of limited duration, or when calculating vessel-wall temperature vs. time. The derivation is presented later on along with a method for estimating the vessel-wall temperature. The time for the first iteration (n = 1) is 0, so, in this example, the calculation actually applies to the second iteration (n = 2).

First, estimate the average specific volume during the temperature increase using the specific volumes from Step 5:

$$\hat{V}_{ave} = \frac{(\hat{V}_{n+1} + \hat{V}_n)}{2} = \frac{\left(0.0527655 \text{ ft}^3 \text{ / lb} + 0.0536716 \text{ ft}^3 \text{ / lb}\right)}{2}$$
$$= 0.0532186 \text{ ft}^3 \text{ / lb} \quad (18)$$

Next, using the vessel volume from Step 1, find the average vessel mass during the temperature increase. Be aware that mass is removed by the relief device, so the vessel mass should be recalculated for each iteration:

$$\text{m} = \text{V} / \hat{\text{V}}_{\text{ave}} = 395.8 \text{ ft}^3 / 0.0532186 \text{ ft}^3 \text{ / lb} = 7,437 \text{ lb} \quad (19)$$

Finally, calculate the time required for the temperature to increase and add it to the calculated time from the previous iteration. This particular calculation is for the second iteration, and the time from the previous iteration is zero. This calculated time is the cumulative time since the onset of the fire:

$$t_{n+1} = t_n + m\frac{\Delta\hat{H}}{Q/60} = 0 + 7,437 \text{ lb} \times$$
$$\frac{189.196 \text{ Btu / lb} - 186.926 \text{ Btu / lb}}{684,800 \text{ Btu / h} \times 1 \text{ h / 60 min}} = 1.5 \text{ min} \quad (20)$$

Step 8: Calculate the isentropic-nozzle mass flux, G. For more information, refer to the orifice-sizing derivation presented later on. Due to choked (or critical) flow, an iterative method may be necessary to find the theoretical mass flux. Find the choked mass flux by maximizing the mass flux:

$$G = \frac{\sqrt{2\left(\hat{H}_0 - \hat{H}_b\right)}}{\hat{V}_b} 3,955.77 \quad (21)$$

subject to the following isentropic constraint:

$$\hat{S}_0 = \hat{S}_b \quad (22)$$

Table 1. *n*-butane mass flux for the example.

T_b, °R	P_b, psia	$\hat{V}_b$, ft^3/lb	$\hat{H}_b$, Btu/lb	$\hat{S}_b$, Btu/lb·°R	G, lb/h·in.^{2}
815.0	982.7	0.05277	186.93	1.2409	0
813.8	963.0	0.05329	186.73	1.2409	46,620
783.2	642.9	0.07135	183.15	1.2409	152,310
781.2	630.1	0.07287	182.99	1.2409	152,350
779.1	617.5	0.07449	182.81	1.2409	**152,390**
777.0	605.1	0.07621	182.63	1.2409	152,110
774.7	593.0	0.07807	182.46	1.2409	151,440

The pressure at which this maximum flux occurs is the choking pressure. The pressure at point b cannot be less than the choking pressure, even if the relief valve backpressure is less than the choking pressure.

To find the choke pressure, first assume that the orifice inlet properties are equivalent to the vessel properties. Ignore choked flow by assuming that the orifice outlet-pressure is equal to the relief-valve backpressure. Next, calculate the mass flux for multiple backpressures by keeping the entropy constant and starting with a backpressure that is equal to the relief-valve inlet pressure. A sample calculation for the first iteration for n-butane is summarized in Table 1, with each backpressure representing a 2% decrease in the gage pressure. Once the maximum mass flux is found, the choked condition has been solved and no further calculations are required. When generating these mass flux values, the property package should be set up to indicate two-phase flow of the fluid being relieved.

To calculate physical properties for Table 1, refer to Step 5. The following sample calculation shows the mass flux calculation for the choked flow condition of Table 1:

$$G = \frac{\sqrt{2\left(186.926 - 182.809\right) \text{ Btu / lb}}}{0.074487 \text{ ft}^3 \text{ / lb}}$$
$$\times 3,955.77 \frac{\text{lb}}{\text{in.}^2 \cdot \text{h}} \frac{\text{ft}^3}{\sqrt{\text{Btu} \cdot \text{lb}}} = \frac{152,390 \text{ lb}}{\text{h} \cdot \text{in.}^2} \quad (23$$

Table 2. n-butane relief-rate for the example.

t, min	T, R	$\hat{V}$, ft³/lb	$\hat{H}$, Btu/lb	$\hat{S}$, Btu/lb·R	$\dot{V}$, ft³/h	$\dot{m}$, lb/h	G, lb/h·in.²	A, in.²
0.0	815	0.05277	186.93	1.2409	273.3	5,180	152,390	0.03486
1.5	817	0.05367	189.20	1.2437	282.3	5,261	149,320	0.03613
9.9	829	0.05976	202.93	1.2604	331.1	5,541	132,740	0.04282
11.2	831	0.06086	205.21	1.2631	338.1	5,555	130,450	0.04368
12.5	833	0.06198	207.47	1.2659	344.7	**5,562**	128,180	0.04450
13.7	835	0.06312	209.73	1.2686	351.0	5,561	126,110	0.04523
15.0	837	0.06427	211.98	1.2713	356.9	5,554	124,210	0.04586
23.7	853	0.07375	229.35	1.2918	391.5	5,309	111,950	0.04864
24.7	855	0.07495	231.45	1.2943	394.3	5,262	110,800	0.04870
25.6	857	0.07614	233.52	1.2967	396.9	5,212	109,680	**0.04874**
26.6	859	0.07733	235.58	1.2991	399.1	5,161	108,680	0.04871
27.5	861	0.07852	237.61	1.3015	401.1	5,109	107,730	0.04864
33.3	875	0.08667	251.40	1.3174	408.2	4,710	102,230	0.04725
34.0	877	0.08781	253.31	1.3195	408.4	4,651	101,600	0.04695
34.8	879	0.08894	255.20	1.3217	**408.4**	4,592	100,990	0.04664
35.5	881	0.09006	257.07	1.3238	408.3	4,533	100,410	0.04631
36.2	883	0.09117	258.94	1.3259	408.0	4,475	99,830	0.04597

From the table, choked flow occurs near 779.1°R and 617.5 psia. If the relief valve backpressure is greater than this choking pressure, then the theoretical mass flux for the relief valve is equal to the calculated mass flux at that backpressure. If the backpressure is less than this choking pressure, then the relief valve is choked and the theoretical mass flux is equal to the calculated mass flux at the choked condition. Flow will normally be choked, since the choking pressure is typically greater than 50% of the relief-valve set pressure (gage), while the relief-valve backpressure is typically less than 10% of the set pressure for conventional valves, and 30–50% for bellows valves *(5)*. In this example, the backpressure is assumed to be less than 10% of the set pressure (94.7 psia). This is well below the choking pressure (617.5 psia), so that the flow is choked and the theoretical mass flux is approximately 152,390 lb/h·in.²

Step 9: Calculate the orifice area, A.

More on the orifice area and the effective coefficient of discharge is presented at the end of this article. Based on the theoretical mass flux and the required relief rate, the required orifice area can finally be calculated. To correct this calculation for system nonidealities, use the derating factors from Ref. 5 for the backpressure, use of a rupture disc, discharge coefficient, and viscosity. A conventional valve is chosen with a backpressure of less than 10% of set pressure, so K_b = 1.0. A rupture disc is not used in the system, therefore, K_c = 1.0. The effective coefficient of discharge for the vapor is assumed, yielding K_d = 0.975. Normally, no viscosity correction is required for a supercritical fluid, thus, K_v = 1.0.

From Steps 6 and 8, the required relief rate for the initial case is 5,180 lb/h and the theoretical mass flux is 152,390 lb/h·in.² The area is then:

$$A = \frac{\dot{m}}{G\,K_b\,K_c K_d K_v} = \frac{5{,}180 \text{ lb/h}}{152{,}390 \text{ lb/h}\cdot\text{in.}^2 \times 1 \times 1 \times 0.975 \times 1} = 0.03486 \text{ in.}^2 \quad (24)$$

Step 10: Tabulate the results. Summarize the calculations for each temperature iteration by adding a row to a results table. Once all iterations are complete (refer to Step 11), the table will take the form of Table 2. This table is truncated to show the first two calculation steps, plus the steps leading to the largest mass relief-rate, the largest required orifice-area, and the largest volumetric relief-rate.

Step 11: Are $\dot{m}$, $\dot{V}$ and A decreasing? Determine if the procedure is complete. In most cases, the relief-valve sizing is complete when the required mass and volumetric relief-rates, as well as the required orifice area, all decrease from the previous iteration. However, further iterations may be needed, since the orifice area may begin to increase again or if the vessel-wall temperature is being modeled for a specific time interval. The orifice area may increase again if the fluid is a liquid and has not reached supercritical conditions, since a supercritical fluid typically has a greater expansion rate than does a liquid. Not all of these cases can be identified, and some engineering judgment may be required to determine if the relief-valve sizing is complete. The criteria presented here serve only as guidelines.

If the iterations are complete, skip to Step 13. If additional iterations are required, proceed to Step 12.

Step 12: Calculate the temperature for the next iteration, T. This is required when further iterations are needed to complete the dynamic relief-valve model. The temperature must be increased for the next iteration of vessel-fluid temperature since boiling does not occur to limit

the temperature, which will continue to rise as long as heat is added. The calculation shown here is the last step for the first iteration of the *n*-butane example; $T_{n+1} = T_n + \Delta T$ = 815°R + 2°R = 817°R. This temperature is not the vessel-wall temperature. Refer to the relief-rate derivation presented later on if an estimated wall temperature is required. Once the temperature is calculated for the next iteration, return to Step 3.

Step 13: Select the relief-valve orifice size. Proceed to this step only when all of the iterations are complete. The required relief valve area is the maximum required orifice area, *A*, from the table generated in Step 10. For the example, the maximum required orifice area from Table 2 is 0.04874 in.^{2} and a D orifice per API 526 *(10)* is therefore selected.

Required relief-rate derivation

The basis is presented here for calculating the required relief-rate for heat input with no boiling present. The method is similar to that summarized in Ref. 4 and is based on the same main assumptions: there are no temperature gradients in the vessel and mass does not exit the system except through the relief device. The first assumption is conservative with respect to the required orifice area, since the worst-case expansion temperature is assumed throughout the vessel. In reality, heat is transferred by natural convection of the vessel contents, during which heat is removed from the wall. This takes place more slowly than heat-removal boiling, and can lead to thermal gradients across the contents, an excessive wall temperature and eventual vessel failure. The vessel wall may require additional temperature protection as discussed in API 521, Section 3.15 *(3)*. If necessary, approximate the vessel-wall temperature by assuming that heat transfer occurs predominantly by natural convection from the wall to the contents *(4)*.

The required relief rate is derived using the definition of specific volume:

$$V = m\hat{V} \tag{25}$$

Evaluating the derivative as a function of time shows the volumetric growth of the fluid that is absorbing the heat. This volume increase must be vented since the vessel's volume is virtually constant. Although mass leaves the vessel, the mass of the fluid expanding is treated as constant. Additionally, the vessel relief-pressure is assumed to be constant. Thus:

$$\text{Required relief rate } = \dot{V} = \frac{dV}{dt} = m\frac{d\hat{V}}{dt} \tag{26}$$

The volume increases due to the heat input from the fire or other relief case. The energy balance for the expanding fluid is shown below. Again, the relief pressure and fluid mass are treated as constants.

$$Q = m\frac{d\hat{H}}{dt} \tag{27}$$

Combining Eqs. 26 and 27 eliminates mass and time. The physical properties are taken across the constant relief pressure:

$$\dot{V} = Q\left.\frac{d\hat{V}}{d\hat{H}}\right)_P \tag{28}$$

The differential expansion term is approximated to simplify calculations:

$$\dot{V} = Q\frac{\Delta\hat{V}}{\Delta\hat{H}} \tag{29}$$

The mass relief-rate is then related to the volumetric relief-rate by the specific volume:

$$\dot{m} = \dot{V} / \hat{V} \tag{30}$$

Eqs. 29 and 30 form the basis for Step 6. Eq. 28 is similar to Eq. 1 in API 521, Section 3.14.3 *(3)*, which is used to describe the thermal expansion of a liquid. However, the specific volume and enthalpy are typically easier to obtain from property packages. Eq. 29 would also be applicable to a boiling-liquid if using the saturated properties and taking credit for the liquid volume removed by boiling. However, this credit is typically ignored and the mass relief-rate for a boiling liquid reduces to the more familiar equation of the heat input divided by the latent heat *(3)*.

For a boiling liquid, the specific volume and enthalpy changes are distinct steps in the transition from saturated liquid to saturated vapor. For single-component systems, these steps occur with no temperature change, mandating that the specific heat and cubical expansion are infinite for the phase transition. Theoretically, a similar phenomenon may occur at the critical point, except with no visible phase change.

The heating time for Step 7 is derived from Eq. 27 by approximating the differential, solving for time, and adding unit consistency:

$$t_{n+1} = t_n + m\frac{\Delta\hat{H}}{Q / 60\ \text{min/h}} \tag{31}$$

Relief orifice-area basis

The theoretical basis for calculating the required orifice area is presented here. The theory of compressible flow through an orifice or nozzle is well-documented, based upon adiabatic, isentropic flow, combined with a simplified energy balance. Thermodynamics textbooks cover the theory in more depth *(11)*. However, most practical engineering applications rely upon an ideal-gas simplification to calculate choked-flow behavior. Nonetheless, supercritical relief deviates significantly from such behavior. Before proceeding with finding the orifice area, we shall review the compressible flow of real and ideal gases through an orifice. Additionally, since the flow is com-

pressible, choked flow will be reviewed. The starting point is the entropy and energy balance equations that describe basic nozzle flow.

Minimal heat is added or removed from the nozzle and the flow is nearly frictionless. This means that the flow is essentially adiabatic and reversible, which equates to isentropic flow:

$$dS = \frac{dQ_{rev}}{T} = 0 \qquad (32)$$

The fluid energy balance for adiabatic, frictionless nozzle flow is also well-known:

$$d\hat{H} + vdv = 0 \qquad (33)$$

The velocity term from Eq. 33 is a measure of the kinetic energy, while the enthalpy term combines the internal energy with the pressure-volume energy. Ignoring choked flow for the moment, the pressure drop across the orifice lowers the fluid's enthalpy and increases its velocity. Integrating Eq. 33 and adding unit consistency results in:

$$v_b = v_o + \sqrt{2 \times \left(\hat{H}_o - \hat{H}_b\right) \times 25{,}037 \text{ lb - ft}^2 / \text{s}^2 / \text{Btu}} \qquad (34)$$

Since no mass flows through the orifice until the enthalpy decreases, the initial velocity is zero and the initial enthalpy is that upstream from the orifice, in this case the vessel.

Eq. 34 is valid until the sonic velocity is reached at the choked condition. The terms "choked" and "critical" are synonymous, but "choked" is used here to avoid confusion with the term "supercritical." Choked flow occurs when an additional pressure drop no longer increases the mass flux. The mass flux through the orifice is simply the flow velocity divided by the specific volume, as shown by Eq. 35 (with added unit consistency):

$$G = \frac{v_b}{\hat{V}_b} \times \frac{1\,\text{ft}^2}{144\,\text{in.}^2} \times \frac{3{,}600\,\text{s}}{1\text{ h}} \qquad (35)$$

Combining Eqs. 34 and 35 yields Eq. 36, the simplified form used here:

$$G = \frac{\sqrt{2\left(\hat{H}_0 - \hat{H}_b\right)}}{\hat{V}_b} \times 3{,}955.77 \frac{\text{lb}}{\text{in.}^2 \cdot \text{h}} \frac{\text{ft}^3}{\sqrt{\text{Btu} \cdot \text{lb}}} \qquad (36)$$

Also, as in Eq. 32, the flow is isentropic:

$$\hat{S}_0 = \hat{S}_b \qquad (37)$$

Eq. 36, subject to the constraints of Eq. 37 and choked-flow theory, is the basis for the relief-valve orifice-flow in Step 8. As mentioned before, choked flow occurs when a further pressure drop no longer increases the mass flux. Using Eq. 35, an additional pressure drop simply begins to increase the specific volume at a faster rate than the velocity increases and the calculated mass flux reaches a maximum. The choked condition is found by calculating the mass flux as a function of multiple isentropic relief-valve backpressures, or by taking the derivative of the mass flux with respect to pressure at constant entropy, setting it at zero, and solving the expression.

For this supercritical relief method, the first method is selected so the mass flux is calculated for multiple pressures, and the choked condition is found at the maximum mass flux. If the relief-valve backpressure is greater than the choking pressure, then Eq. 36 is valid for flow through the orifice. If the relief-valve backpressure is less than the choking pressure, then the flow is choked and the mass flux equals the choked mass flux. Refer to the example in Step 8.

The mass flux found by this method is based on a theoretical model that should be corrected for system non-idealities. In a manner similar to the Leung omega method *(5, 7)*, the derating factors from API 520, Part I *(5)* are assumed to apply to supercritical relief. Eq. 38 becomes the basis for calculating the required orifice area for Step 9 of the procedure:

$$A = \frac{\dot{m}}{G\ K_b K_c K_d K_v} \qquad (38)$$

As stated in API 520 Part I, there are no recognized procedures for certifying the capacity of pressure-relief valves in two-phase service. This is suspected to be true for supercritical fluids. These fluids have the characteristics of both liquids and vapors, which adds further complexity. Since compressible flow theory is used to calculate the mass flux for the example, the effective coefficient of discharge for the vapor (K_d = 0.975) is assumed. The accuracy of this assumption is currently unknown. See API 520, Part I, Section 3.2 for additional details on K_d.

This method for determining the orifice area is tedious and leads to numerous calculations. For this reason, some alternative orifice-sizing methods follow. The discussion includes some basic observations about the methods relative to supercritical relief. These methods typically apply to orifice sizing (Steps 8 and 9) and may not include relief-rate methods.

Alternative orifice-sizing methods

Four alternatives are examined for calculating the orifice area. They typically apply to the orifice-sizing steps and may not include relief-rate methods. The first is sizing per API 520, Part I, Section 3.6 *(5)*. This standard discusses the ideal-gas limitation to these equations in its Appendix B. This limitation sufficiently describes a non-ideal, supercritical fluid, so the equations from Section 3.6 are not recommended for a supercritical fluid unless the modifications from Appendix B are used. This appendix presents a simplified relief-valve-sizing method for real gases based on equation-of-state thermodynamics along the isentropic relief path. The procedure presented here uses a similar thermodynamic and relief-path basis, except with a more-rigorous model.

Another API-recommended method is found in API

521, Section 3.15.2.1.2 *(3)*. This one is based on ideal-gas properties, the physical properties of air, no change in fluid temperature, and an uninsulated vessel with no mass. Section 3.15.2.2 then suggests that a more-rigorous method, such as in Ref. 4, may be required when these assumptions are not appropriate. This procedure presented here is similar to that in Ref. 4, but with the added benefit of built-in orifice sizing.

A third procedure is the Leung omega method *(7)*. The suggestion is made that the omega factor from Ref. 7 can be calculated for a supercritical fluid with an isentropic (or isenthalpic) depressurization equal to 70% of the relief pressure. Omega characterizes the fluid's expansion relative to an ideal, isothermal gas and is usually greater than unity for a supercritical fluid, since depressurization typically increases the compressibility factor. Using this method may be valid when omega is relatively constant, which essentially amounts to a linear approximation of the compressibility factor as a function of pressure. The method requires only one isentropic calculation, or even an isenthalpic calculation, and is simpler than the procedure presented here. A check may be needed to recalculate omega at the predicted choking pressure, rather than at 70% of relief pressure, to evaluate the extent of change in omega, mass flux and orifice area. This would require a second isentropic calculation.

The last method for calculating the area is the use of the generalized charts from Ref. 6. These charts show that the mass flow of a supercritical fluid can be significantly higher than for an ideal gas ($Z = 1$). This suggests that using the ideal-gas formulas in API 520, Part I *(5)* should normally yield a conservative orifice area at relatively low reduced pressure and temperature, when using a compressibility factor of 1 ($Z = 1$). These charts from Ref. 6 may lead to mass fluxes similar to the ones calculated here, since both depend upon generalized properties and isentropic-nozzle flow. With additional calculations, the entire relief-valve sizing procedure for the fire-case orifice-area may perhaps be generalized. However, the charts may be limited to cases with constant heat input.

Two-phase relief flow

An interesting two-phase phenomenon can occur during supercritical relief. As the pressure decreases isentropically, the relief path can pass into the two-phase region of the fluid. During the mass-flux calculation, the selected property method should be set up to indicate if the fluid has entered the two-phase region. If so, the superheated vapor has depressurized into a saturated vapor, and may eventually precipitate some saturated liquid. The saturated liquid may flash off when depressurized further, allowing the vapor to return to the superheated state. This can occur because the saturated vapor entropy and enthalpy typically decline when approaching the critical point. This can be seen in numerous entropy-pressure diagrams and tables. To use this procedure, the physical properties of the two distinct phases must be combined into a single value, as required for calculations. One method of doing this is the homogeneous equilibrium model (HEM), which assumes equilibrium of the two phases with no slip flow, and is the basis of the Leung omega method. A discussion of HEM is found in Ref. *7*. Leung's method is included in the 7th ed. of API 520, Part I *(5)* as a potential two-phase sizing scheme. However, the reader is cautioned that two-phase relief-valve sizing is still evolving and current recommended practices might be replaced with other ones. Always refer to latest API guidelines. CEP

Literature Cited

1. **Perry, R. H., and Don W. Green, eds.,** "Perry's Chemical Engineers' Handbook," 7th ed., McGraw-Hill, New York, pp. 22-14 to 22-19 (1997).
2. **Lee, B. I., and M. G. Kesler,** "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States," *AIChE J.*, **21** (3), pp. 510–527 (May 1975).
3. "Guide for Pressure-Relieving and Depressurizing Systems," API Recommended Practice 521, 4th ed., American Petroleum Institute, Washington, D.C. (Mar. 1997).
4. **Francis, J. O., and W. E. Shackelton,** "A Calculation of Relieving Requirements in the Critical Region," in *Proc. – Refining Dept.*, **64**, American Petroleum Institute, Washington, D.C., pp. 179-182 (1985).
5. "Sizing, Selection, and Installation of Pressure-Relieving Devices in Refineries, Part I - Sizing and Selection," 7th ed., API Recommended Practice 520, American Petroleum Institute, Washington, D.C. (Jan. 2000).
6. **Leung, J. C., and M. Epstein,** "A Generalized Critical Flow Model for Nonideal Gases," *AIChE J.*, **34** (9), pp. 1568–1572 (Sept. 1988).
7. **Leung, J. C.,** "Easily Size Relief Devices and Piping for Two-Phase Flow," *Chem. Eng. Progress*, **92** (12), pp. 28–50 (Dec. 1996).
8. "API Technical Data Book – Petroleum Refining," API Refining Dept., Chapters 1 (1997), 4 (1987), 5 (1994), 6 (1984), 7 (1992), American Petroleum Institute, Washington D.C.
9. **Moss, D. R.,** "Pressure Vessel Design Manual: Illustrated Procedures for Solving Every Major Pressure Vessel Design Problem," p. 224, Gulf Publishing, Houston, TX (1989).
10. "Flanged Steel Pressure Relief Valves," 4th ed., API Standard 526, American Petroleum Institute, Washington, D.C. (June 1995).
11. **Smith, J. M., and H. C. Van Ness,** "Introduction to Chemical Engineering Thermodynamics," 4th ed., pp. 220–225, McGraw-Hill, New York (1987).

RYAN OUDERKIRK is a process engineer with the Energy & Chemicals unit of Fluor Corp. (100 Fluor Daniel Drive, Greenville, SC 29607; Phone: (864) 281-8656; Fax: (864) 676-7211; Email: ryan.ouderkirk@fluor.com). His projects have included conceptual, front-end, detail and plant engineering design, as well as commissioning and start-up of a process unit based on new technology. His design experiences have included viscous fluids, fluids near their critical point, and a pilot-plant scale-up. He received his bachelor's degree from the Georgia Institute of Technology.

Thank you to my coworkers at Fluor who helped with editing and content, and a very special appreciation to my father, Andrew.