Designing for pressure safety valves in supercritical service

Use this rigorous method to prevent over-sizing

R. C. DOANE, S&B Engineers and Constructors Inc., Houston, Texas

Pressure safety valves (PSVs) on vessels containing liquid hydrocarbon that may be blocked in during a fire can relieve a supercritical fluid, if the relieving pressure is higher than the critical point. The conventional method for calculating an orifice size is presented in API RP-521.[1] This method, however, treats all "un-wetted" vessels the same, whether the fluid contained is supercritical, a vapor or a gas. Caution is given in the API text and states that the given equations are based on the physical properties of air and the perfect gas laws with no change in fluid temperature. The reader is cautioned to review these assumptions to "ensure they are appropriate for any particular situation."

Supercritical fluids are not obedient to the perfect gas laws. Compressibility factors can range from 0.5 to 0.7 and are not constant while the vessel is relieving. Also, the fluid temperature is not constant. Fortunately, it can be shown that the API method is conservative, producing larger orifice areas than required. On the other hand, an over-sized valve has two problems: there is a potential for destructive valve "chatter" and larger PSVs are more expensive.

The method presented adheres to basic thermodynamic principles, not the perfect gas laws. The resulting orifice areas are significantly smaller than those derived from the API method. Sonic flow through the PSV orifice is taken into account.

Fire case scenario. Fig. 1 illustrates a typical fire case situation for a pressure vessel containing a hydrocarbon liquid. Both the inlet and outlet lines have a valve capable of being closed, inadvertently or not. If all the valves are shut, this is considered a "blocked in" condition. The vessel is only 10 ft from grade level. According to the API RP-521 standard, the entire vessel can be exposed to an external fire. The pressure in the drum will rise until the PSV set pressure is reached. At this point, the PSV will start to open. The valve will be fully open at the relieving pressure, normally 21% above the set pressure for a fire case design.

The relieved fluid condition depends on the critical pressure's relation to the relieving pressure. If the relieving pressure is less than the fluid's critical pressure, the liquid will boil when the PSV opens. Relieving pressure will continue until the liquid is all vaporized. The temperature will only vary during the relieving process if the fluid is multi-component having a boiling range.

If the relieving pressure is above the critical pressure, the liquid will not boil. The fluid becomes supercritical, having the properties of one phase, somewhere between a liquid and a vapor. The fire will continue to heat the drum and its contents, even if the fluid is composed of only one compound. Eventually the pressure will reach the PSV relieving pressure. The PSV will open and relieve a vapor below the critical pressure. Relieving pressure will continue until no more moles of fluid remain in the drum to maintain the pressure.

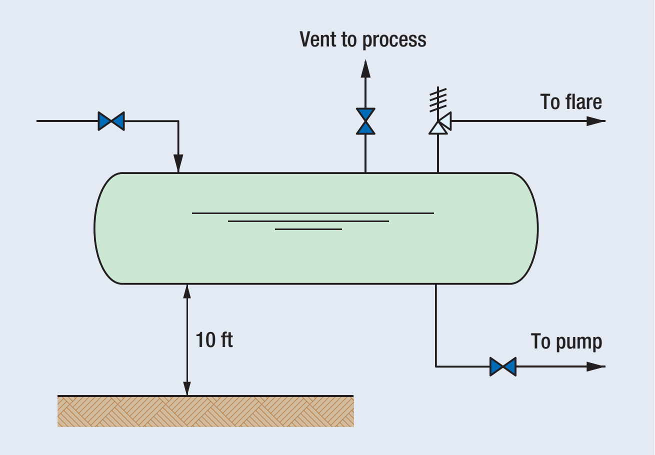

FIG. 1 Typical vesssel subject to fire case study (and possibly supercritical relief).

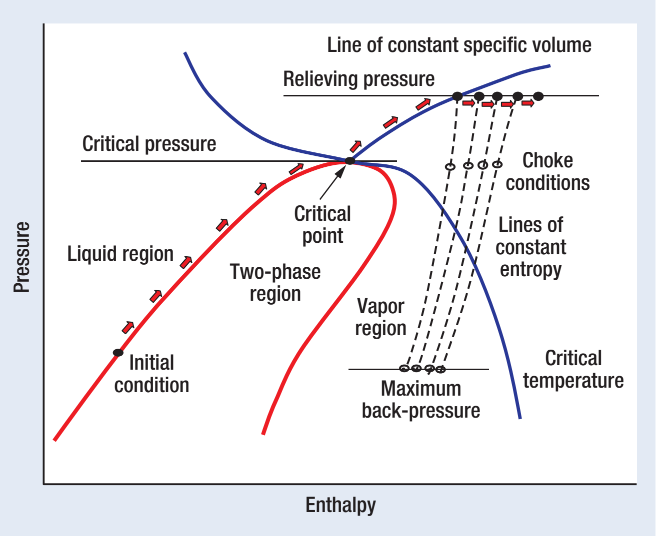

FIG. 2 Typical hydrocarbon P-H Diagram (showing path of fluid conditions into the supercritical).

TABLE 1. Supercritical relief valve sizing example problem—normal butane

Segment points	Point number	T (F)	P (psia)	*rho* (lb/ft³)	V (ft³/lb)	Enthalpy h (Btu/lb)	Entropy s (Btu/lb-F)	Cp/Cv k	Choked pres Pc (psia)	Choked flow ?	Orifice velocity v (ft/sec)	Mass flux G (lb/ft²sec)	Volume flow Q (ft³/hr)	Mass flow W (lb/hr)	Orifice area A (sq in.)
	critical	306	550	10.74	0.0931										
1 to 2	1_{in}	424.0	983	10.74	0.0931	–815.8	0.5797	1.522	499.9	yes	953	4,658	1,304	6,374	0.0644
	1_{sonic}	359.0	499.9	4.889	0.2045		0.5797	1.295							
	1_{subout}	200.8	40.0	0.3430	2.9155	–881.7	0.5797								
2 to 3	2_{in}	434.0	983	10.19	0.0981	–807.0	0.5896	1.464	508.9	yes	950	9,685	1,315	1,3405	0.0651
	2_{sonic}	372.3	508.9	4.775	0.2094		0.5896	1.268							
	2_{subout}	214.3	40.0	0.3352	2.9833	–875.1	0.5896								
3 to 4	3_{in}	444.0	983	9.711	0.1030	–798.6	0.5990	1.415	516.8	yes	949	9,219	1,274	12,371	0.0631
	3_{sonic}	385.0	516.8	4.671	0.2141		0.5990	1.246							
	3_{subout}	227.3	40.0	0.3281	3.0479	–868.6	0.5990								
4 to 5	4_{in}	454.0	983	9.293	0.1076	–790.3	0.6081	1.375	523.5	yes	949	8,819	1,250	11,620	0.0620
	4_{sonic}	397.4	523.5	4.57	0.2188		0.6081	1.227							
	4_{subout}	239.8	40.0	0.3216	3.1095	–862.3	0.6081								
	5_{in}	464	983	8.925	0.1120	–782.2									

Vessel diameter (ft):	6			T_{normal}	90	F
Vessel tan-tan (ft):	12	Molecular weight:	58.12	P_{normal}	44	psia
A_e (exposed area) (sq ft)	304	Relieving pressure (psia)	983	Kd	0.85	(2)
f (insulation factor)	1.0	= found by trial		Kb	1	
q (mBTU/hr)	2.283 (5)	Back-pressure, Pa (psia)	40	Kc	1	

The path to supercritical. Fig. 2 shows a pressure-enthalpy (P-H diagram) to illustrate the path taken by the fluid from the initial condition to the relieving condition—after the drum is blocked in and a fire starts. The vapor remains in equilibrium as the temperature increases.

The pressure follows the liquid's vapor pressure up the boundary of the two-phase region to the critical point. If the relieving pressure is above the critical point, the pressure and temperature will continue to increase along the path of constant specific volume, from the critical point to the horizontal relieving pressure line. The fluid must remain at constant volume because, with no fluid relief, both the mass of fluid and the vessel volume remain essentially constant. The distinction between vapor and liquid phases has been lost.

After reaching the relieving pressure, the fluid will continue to be heated by the fire. The pressure must remain the same to avoid over-pressuring the drum. The temperature and required relieving rate will vary as the relieving process continues.

Fig. 2 also shows five points, corresponding to different PSV inlet conditions along the relieving pressure line. These points will be needed to verify location of the condition requiring the largest PSV orifice area. It has been shown that the mass relieving rate, volume relieving rate and maximum orifice area are not necessarily found at the same temperature.[3]

Also illustrated are four points corresponding to a choked condition at the outlet of the orifice. The velocity through the orifice is sonic for these conditions and the relieving rate must be calculated accordingly. Sonic flow is typical for supercritical relief. The remaining four points, along the back-pressure line, are only needed when the orifice flow is *not* sonic.

Procedure and calculations. The procedure consists of transcribing property data obtained from a process simulator onto a spreadsheet that calculates relieving rates and required orifice areas (Table 1). The calculations follow the logic diagram in Fig. 3. The fluid in this example is normal butane. The vessel is assumed to be essentially full, with a small vapor space. Table 2 shows the fluid and vessel data that should be gathered and entered into the spreadsheet.

TABLE 2. Fluid and vessel information gathered and inputted into the spreadsheet

Data required	Comment
Vessel exposed area	Include both heads
Insulation factor	Usually 1.0; see Table 5 in API RP-521 § 3.15
PSV relieving pressure	For a fire case, the relieving pressure is 1.21 times the set pressure.
Maximum PSV back pressure	The flare system is usually designed to provide a maximum value at each PSV
Fluid mole weight and critical properties	The process simulator may be needed to calculate the critical properties.

TABLE 3. API RP-521 method vs. the rigorous method

Method	Max. orifice area (in.²)	Relief mass rate (lb/hr)	Orifice velocity (ft/sec)
API RP-521	0.186	14,351	287
Rigorous	0.0651	13,405	950

To calculate the heat transfer rate from a fire, use Eq. 1:[1]

$$Q = 21,000\, f A_e^{-0.18} \quad (1)$$

It is assumed that Eq. 1, derived for wetted surface areas, is also applicable for supercritical fluids, where the concept of "wetted" becomes nebulous. Any error is on the safe side, since the heat transfer rate to a wetted surface is higher than for an unwetted surface.

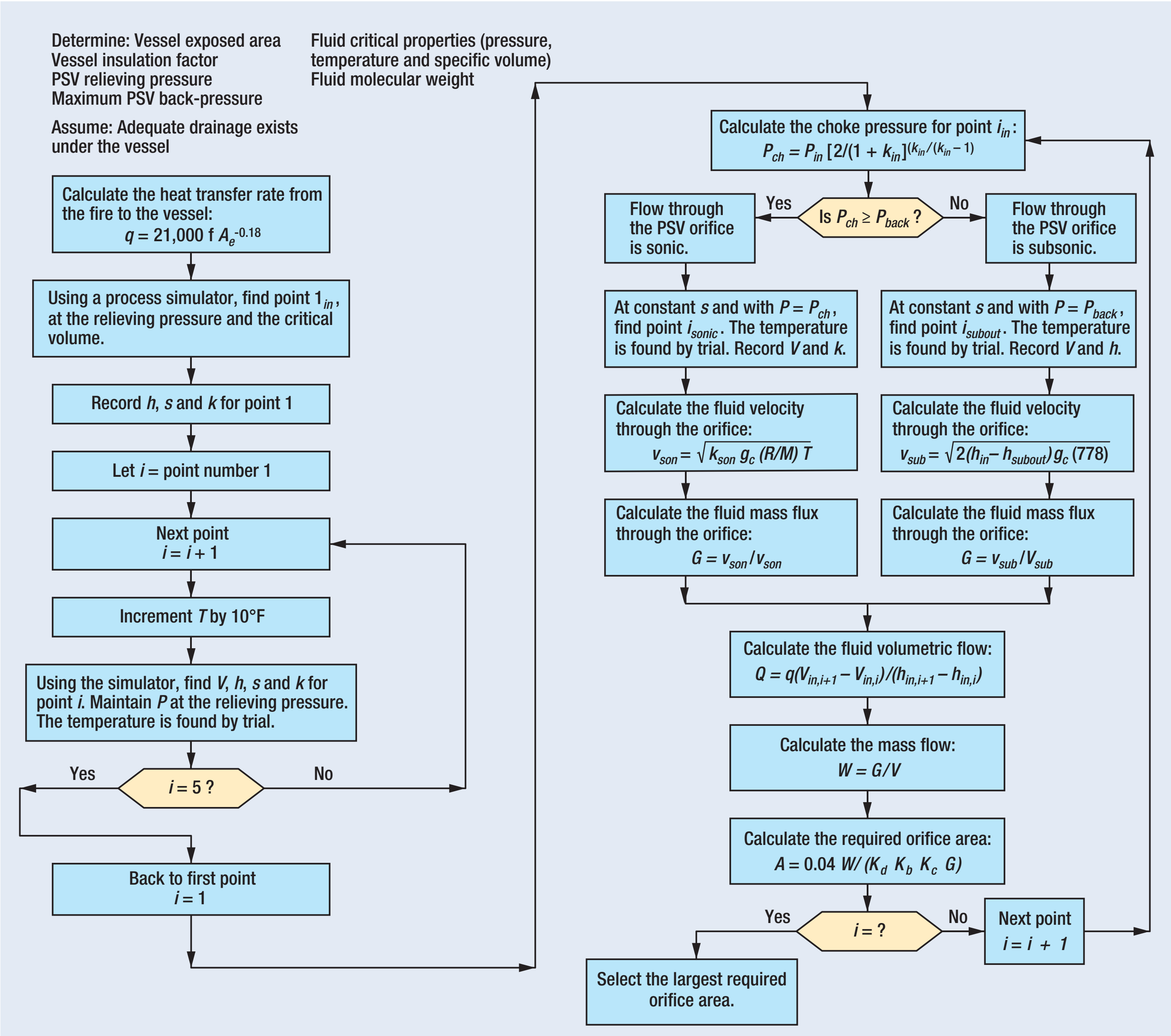

FIG. 3 Logic diagram for supercritical relief valve sizing.

Using a simulator program, define the first point 1_{in}, on the relieving pressure line. The specific volume must equal the fluid's critical volume. Knowing *P* and *V*, find *T* by trial. This is equivalent to drawing a line of constant specific volume from the critical point to the horizontal relieving pressure line. Record *h*, *s* and *k* for point 1_{in}.

Move to the next point by incrementing *T* by 10°F. A higher accuracy can be achieved with smaller temperature increments, but 10° is sufficient for this example. Knowing *P* and *T*, use the simulator to find *V*, *h*, *s* and *k* for point 2_{in}. Repeat the temperature increments until all five PSV inlet pressures have been defined.

For each point it must be known whether or not the flow through the orifice is sonic. The choke pressure at the orifice is calculated from Eq. 2.[4]

$$P_{ch} = P_{in}[2/(1+k_{in})]^{(k_{in}/(k_{in}-1))} \quad (2)$$

Compare P_{ch} with P_{back}. If the choke pressure is higher than the back-pressure, sonic flow exists at the orifice.

Sonic flow. Since the change in condition from upstream of the orifice to the orifice itself is adiabatic and almost reversible, the change is virtually isentropic. We can determine the other properties for i_{sonic} by keeping *s* the same as for the inlet point, i_{in} and setting $P = P_{ch}$. The temperature is found by trial. This is equivalent to drawing an isentropic line from point i_{in} to P_{ch} on the P-H diagram. Record k_{sonic} and *V*.

The sonic velocity is found using Eq. 3:[4]

$$v_{son} = \sqrt{k_{son} g_c (R/M)T} \quad (3)$$

The orifice area equation will need a value for the mass flux, *G*, found from the velocity and specific volume:

$$G = v_{son} / V_{son} \quad (4)$$

Subsonic flow. For subsonic flow, the procedure and equations are similar to the sonic case. At constant s and with $P = P_{back}$, define point i_{subout}. The temperature is found by trial. This is equivalent to drawing an isentropic line from i_{in} to the back-

The PSV discharge coefficient is assumed to be 0.85, as recommended in the API RP-521 standard for preliminary sizing when vendor data is unavailable. The back pressure is normally 1 for supercritical relief, since the relieving pressure is so high.

pressure line on the P-H diagram. Record *h* and *V*.

The subsonic velocity can be found using Eq. 5, derived from the first law of thermodynamics, neglecting the relatively low velocity upstream of the orifice.[4]

$$v_{sub} = \sqrt{2(h_{in} - h_{subout})g_c(778)} \quad (5)$$

The mass flux equation for the subsonic case is very similar to that of the sonic case. Note that the subscripts in Eq. 6 are not the same as in Eq. 4.

$$G = v_{sub} / V_{sub} \quad (6)$$

Perform the velocity and mass flux calculations, including the sonic/subsonic flow analysis, for each point 1 through 4.

Orifice sizing. After calculating *G* for each of points 1 through 4, the fluid volumetric flow is found using Eq. 7.

$$Q = q(V_{in,i+1} - V_{in,i}) / (h_{in,i+1} - h_{in,i}) \quad (7)$$

This is an approximation to the differential equation resulting from a heat and mass balance around the vessel, with constant relieving pressure:[3]

$$Q = q(dV/dh)_p \quad (8)$$

Knowing *Q* and *G*, the mass relieving flow and required orifice area are found from Eqs. 9 and 10 as follows:[2]

$$W = G/V \quad (9)$$

$$A = 0.04W/(K_d K_b K_c G) \quad (10)$$

The PSV discharge coefficient is assumed to be 0.85, as recommended in the API RP-521 standard for preliminary sizing when vendor data is unavailable. The back pressure correction is normally 1 for supercritical relief, since the relieving pressure is so high. The combination factor is also 1, since a rupture disk is not included in this example.

When the spreadsheet is complete, there are four values for the orifice area to choose from. Simply select the maximum value for the design. In the example spreadsheet, the area for point 2, 0.0651 in.^{2}, is the largest of the four. It may be necessary to define more points and expand the spreadsheet if the maximum area occurs at point 4 or beyond.

Comparison with the conventional method. Table 3 compares the results of the conventional method in the API RP-521 § 3.15 standard with the more rigorous method presented. The results of both methods are based on the previous example problem. For the conventional method, the relieving temperature is the same as for the rigorous method. Using the ideal gas law to find the relieving temperature, as suggested in the API RP-521 standard, may lead to unrealistic results.

It is readily seen that the conventional method in the API RP-521 standard produces conservative results for relief of supercritical fluids. The orifice design size is about three times the area calculated using the more rigorous method. The mass rate is higher, but the orifice velocity is far below sonic.

Conclusion. PSV orifice areas calculated using the method in the API RP-521 standard when relieving supercritical fluids are conservatively large. Orifices sized using a more rigorous approach, based on thermodynamic principles, can be significantly smaller, resulting in cost savings. **HP**

LITERATURE CITED

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NOMENCLATURE

P	Fluid pressure, psia
T	Fluid temperature, degrees Rankine
rho	Fluid density, lb/ft^3
V	Fluid specific volume, ft^3/lb
v	Fluid velocity, ft/sec
h	Fluid specific enthalpy, Btu/lb
s	Fluid specific entropy, Btu/lb-°F
k	Specific heat ratio, Cp/Cv
G	Fluid mass flux, lb/ft^2-sec
W	Fluid mass flow, lb/hr
A	PSV orifice area, in.^{2}
Ae	Surface area of vessel exposed to the fire, ft^2
i	Fluid point number on the relieving pressure line
gc	Newton's law conversion factor, lbm-ft/lbf–sec^2
M	Fluid molecular weight
K_d	PSV discharge coefficient
K_b	PSV back pressure correction factor
K_c	PSV combination correction factor
Q	Fluid volumetric flow rate, ft^3/hr
q	Heat transfer rate from external fire to the fluid, millions of BTU/hr
f	Vessel insulation factor
R	Gas constant, $1,546 \frac{\text{lbs} - \text{ft}}{\text{lb}_{\text{mol}} - °\text{R}}$

SUBSCRIPTS

in	Fluid data at PSV inlet
sonic or *son*	Fluid sonic velocity data at the PSV orifice outlet
subout	Subsonic fluid data at the outlet of the PSV orifice
norm	Normal fluid condition
ch	Choke flow condition

Richard Doane recently retired following 37 years experience in engineering and construction, plant start-up, and operation supervision. When this article was written, Mr. Doane was a senior process engineer with S&B Engineers and Constructors in Houston, Texas. He holds BS and MS degrees in chemical engineering from Northeastern University in Boston, Massachusetts and an MS degree in accounting from the University of Houston in Clear Lake, Texas.