

Calculating Relief Load for Liquids Near Critical Temperature

When a liquid in a process vessel experiences excessive heat input, either due to fire, heat exchange or some other heat source, overpressure of the vessel is possible due to vapor generation from liquid boiling. The current common practice for determining the required vapor relief load for this situation is to divide the heat input by the heat of vaporization:

$$W = \frac{Q}{\lambda} \quad (\text{eq. 1})$$

W = Relief Load (Lb / Hr)

Q = Heat Input (Btu / Hr)

λ = Latent Heat of Vaporization (Btu / Lb)

For the great majority of cases, this provides a reasonably conservative estimate of the vapor flowrate which needs to be relieved to prevent vessel overpressure. However, when relief conditions approach the thermodynamic critical temperature, the latent heat of vaporization rapidly decreases to zero. At boiling conditions near the critical temperature, use of the conventional method, as given in equation 1, results in relatively large relief rates.

Relief rates at near critical temperature using equation 1 are unreasonably conservative. That's because equation 1 is only an approximation to the more general equation:

$$W = \frac{Q}{\lambda} \left[1 - \frac{\rho_v}{\rho_l} \right] \quad (\text{eq. 2})$$

ρ_v = vapor density

ρ_l = liquid density

Equation 2 is the more general relationship. For conditions far from critical, the density ratio is usually much less than one and the ratio correction factor can be ignored. But for conditions near critical, the vapor and liquid densities approach each other and the correction factor becomes significant. Note also, that equation 2 should also be used for systems far from critical when the vapor density can be relatively large. This could occur in high pressure, low temperature, and high molecular weight systems.

What is the rationale behind equation 2? Leung (AIChE Journal, October, 1986, P. 1624) derived a similar relationship using a dynamic heat and material balance for the two-phase boiling system. The analysis is somewhat detailed but it can be explained quite simply. The basis for all relief load estimates is that the volume to be relieved must equal the net volume generated. In a boiling, two-phase system, two volumes exist: the vapor volume and the liquid volume. It is important to emphasize that when a liquid boils, vapor volume is generated but liquid volume is depleted. That liquid volume can be taken up by part of the vapor without any generation of pressure. This is seen from a volume balance:

Volume to be Relieved = Vapor Volume Generated - Liquid Volume Lost

Let's say 100 lbs of liquid is vaporized. If the vapor density is 0.1 lb/ft³, then 1000 ft³ of vapor is formed. If the liquid density is 50 lb/ft³, only 2 ft³ of liquid is depleted. For this case, the liquid volume depleted is very small compared to the vapor volume generated and can be ignored, or equation 1 applies. But near the critical point, the volume lost by the liquid can be significant compared to the volume generated from the vapor since the densities are more comparable. For this case, if the vapor density is 10 lb/ft³, then 10 ft³ of vapor is generated. And if the liquid density is 20 lb/ft³, then 5 ft³ of volume is depleted. That means 5 ft³ of depleted liquid volume is available to 5 ft³ of vapor volume and only 5 ft³ of vapor volume needs to be relieved. Mathematically:

$$\text{Relief Volume} = \frac{Q}{\lambda \rho_v} - \frac{Q}{\lambda \rho_l}$$

Vapor Vol Formed - *Liquid Vol Lost*

and

$$W = \rho_v \text{ times (Relief Volume)}$$

$$= \rho_v \left[\frac{Q}{\lambda \rho_v} - \frac{Q}{\lambda \rho_l} \right]$$

$$= \rho_v \frac{Q}{\lambda} \left[\frac{1}{\rho_v} - \frac{1}{\rho_l} \right]$$

or,

$$W = \frac{Q}{\lambda} \left[1 - \frac{\rho_v}{\rho_l} \right] \quad (\text{eq. 2})$$

The following table for some example molecules shows the potential reductions in estimated relief load when using the more general equation 2:

Temp (°F)	Sat. Press (Psia)	Heat of Vaporization (Btu / Lb)	Reduction Factor
Butane Tcritical = 305 °F			
224	253	106	0.90
242	304	96	0.87
260	362	84	0.82
278	429	68	0.75
296	504	44	0.59

Decane Tcritical = 652 °F			
476	69	96	0.96
512	98	88	0.95
548	135	78	0.92
584	181	66	0.85
620	240	49	0.72

Ethane Tcritical = 90 °F			
8	248	149	0.93
26	321	135	0.90
44	407	119	0.85
62	510	98	0.78
80	631	65	0.62

As the critical temperature is approached, significant reductions in the calculated relief load from the conventional estimate, equation 1, results. This is shown by looking at the "Reduction Factor" in the last column. For example, for butane at 296 °F, use of the more general equation 2 results in an estimated load 0.59 times less than that estimated from equation 1. The approximate equation 1 is overly conservative as the critical temperature is approached. This could also be true for systems not near critical temperature but having high pressure, low temperature, and high molecular weight components. Subsequent reduction in piping pressure drop is even more significant since the pressure drop will be reduced by the reduction factor squared.

The use of the more general, and less conservative, equation 2 can result in significant savings in project capital cost.