# Rigorous calculation of LNG flow reliefs using the GERG-2004 equation of state

Luigi Raimondi
Process Simulation Services – www.xpsimworld.com
Via Galvani 105, 20025 Legnano (MI) - Italy

The design of process safety valves is described in standard procedures such as the API RP520 or the ISO/DIS 4126-10 - draft international standard
Within these procedures, sizing of safety valves for two-phase fluid discharge has received in recent years large attention and has been the subject of numerous technical papers. Working equations are usually derived considering a single component fluid, approximate dependence of the density with the pressure and other approximations.
These approximations, introduced along the mathematical derivations are subsequently ignored, and derived results are not verified whether they are still valid in the extended range of application (such as high pressure systems and multi-component mixtures exhibiting retrograde behaviour, etc.) so approximated, incongruent or even physically unreliable results can be obtained . Instead in the framework of process simulation, more rigorous method for the calculation of relief flow from pressure safety devices can be developed on the basis of thermodynamic equations of state and the calculation of sonic velocity in both single phase and two-phase flows.
In the LNG industry, the recently developed GERG-2004 equation of state represents an important advance in the availability of high accuracy thermodynamic models.
This paper applies the GERG-2004 equation of state to the relief of LNG fluids and compares the results obtained by cubic equations to those generated by the complex GERG-2004 equation of state.

## 1. Introduction

Sizing and verification of pressure relieving systems is one of the key phases of the design of process plants in both refining and chemical industries. The aim is the protection of process equipments and personnel against abnormal conditions like fire or other emergencies; the process engineer must evaluate the mass of the fluid to be relieved and its relevant thermodynamic conditions (composition, temperature and pressure). Fast depressurization of vessels, by means of fluid discharge to blowdown system or atmosphere, is a common way of reducing the consequences associated with pressure increase. Modeling of blowdown and depressurization of process equipments require the analysis and mathematical description of vapor-liquid equilibrium, heat-transfer and fluid dynamics with equations governing open system thermodynamics as well as the calculation of PVT and transport properties. The relief operation is usually

performed in a condition usually defined as ‘choke flow’ or ‘critical flow’, where the velocity of the fluid, discharged through the safety device, becomes equal to the velocity of sound. This approach has been developed by the author in couple of papers.
With the implementation of the GERG-2004 model in the XPSIM framework (a process simulation software with capabilities analogous to HYSYS, ASPEN, etc.), comparison of the results from this equation with respect to more traditional cubic equations, such as the Soave-Redlich-Kwong SRK (Soave, 1972) or Peng-Robinson PR (Peng et al., 1976) models, naturally appeared an interesting topic in the field of safety analysis.

## 2. Homogeneous Two-Phase models

This paragraph summarizes the thermodynamically rigorous method for the calculation of the flow relieved from a pressure safety device. When a compressible fluid like a gas or a vapor is expanded across a nozzle, the velocity increases as the pressure of the fluid decreases to reach the down-stream pressure. For a given fluid and a set of upstream conditions (let us say $T_0$ and $P_0$ ) the mass flowrate increases until a limit speed value is reached.
It can be shown that this limit velocity corresponds to the velocity of the sound at the point. The flowrate determined by this limit velocity is the ‘critical flowrate’ and the ratio of the pressure at the nozzle exit at sonic velocity $\boldsymbol{P_{cf}}$ to the inlet pressure $P_0$ is the critical pressure ratio. For a gas, when an ideal behavior is assumed, the critical flow pressure ratio is given by the relation:

$$R_{cp} = \left[ \frac{2}{k+1} \right]^{\frac{k}{k-1}} \tag{1}$$

where $\boldsymbol{k}$ is the ratio of specific heats. This value, which is usually around 0.5, represents the separation between the critical and subcritical flow and is frequently used as a ‘rule of thumb’ to guess whether the existing downstream pressure can produce a critical flow. When the two phase flow is considered, things are more complicated and various models can be developed. The method presented in Appendix D of the RP520 document (Sizing for two-phase liquid/vapor relief) is based on Leung’s ‘Omega method’ that was originally proposed by Leung (1996). The method may be used for sizing pressure relief valves for either flashing or non-flashing flow, but important cases where a separated liquid phase is generated from an initial vapor phase are not considered.
In general, the derivation of Omega method includes a number of approximations that prevent its general applicability to multicomponent systems at high pressure where retrograde condensation or evaporation may appear. Besides, the mathematical derivation of the Omega method introduces a number of approximations: a) the change of the vapor fraction is not considered along the isentropic path, but only the change of the gas volume is considered; b) the vapor-liquid coexistence curve is described by means of the Clausius-Clapeyron equation that is not valid for multicomponent mixtures. Therefore, the method cannot describe adequately multicomponent mixtures

near their thermodynamical critical point and in the region where retrograde condensation or evaporation occur.

## 3. Critical Flow Calculations

To avoid the limitations related to the API and Omega methods, the author has developed a general algorithm for the calculation of the maximum allowable flowrate discharged through an orifice for a given upstream conditions (Raimondi, 2007 and 2008). This method is fundamentally based on the rigorous evaluation of the sonic velocity using the same equations of state that are applied for the calculation of thermodynamic properties. The procedure is rigorous and the calculated results depend only on the precision of the equations of state used for the generation of the thermo-physical properties.

The method may be applied without limitations to multi-component and multiphase systems. The limit critical pressure is calculated by finding the pressure at which the fluid velocity takes a value equal to the local sonic velocity.

Inlet conditions are defined by fluid pressure $\boldsymbol{P_0}$, temperature $\boldsymbol{T_0}$, total composition $\mathbf{z}$, molecular weight $\boldsymbol{M_w}$, enthalpy $\boldsymbol{H_0(T_0,P_0,z)}$ , entropy $\boldsymbol{S_0(T_0,P_0,z)}$ and by the initial fluid velocity $\mathbf{v_0}$.

The flowing fluid is characterized by its velocity $\mathbf{v}$., enthalpy $\boldsymbol{H(T,P,z)}$, entropy $\boldsymbol{S(T,P,z)}$ and by the local sonic velocity $\boldsymbol{c=c(T,P,z)}$. The critical flow condition is therefore defined by the following system of equations written for a unit mass of fluid:

$$H_o(P_0,T_0,\mathbf{z})/M_w = H(P,T,\mathbf{z})/M_w + \frac{v^2}{2} \tag{2}$$

$$S_o(P_0,T_0,\mathbf{z}) = S(P,T,\mathbf{z}) \tag{3}$$

$$v \le c(P,T,\mathbf{z}) \tag{4}$$

Equation (4) defines the sonic velocity at flowing conditions defined by:

$$c = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_S} \tag{5}$$

The solution of equations (2) and (3) only, by maximizing the fluid flowrate does not assure that equation (4) is satisfied.

The numerical or analytical derivation of the sonic using the most common equations of state speed is described by the author in a previous paper (Raimondi, 2006).

The solution of the above system of equations (2-4) is obtained by means of a trial and error procedure. Starting from the inlet pressure, successive pressure values are generated to obtain a fluid velocity that equals the sonic velocity calculated at the same pressure.

## 4. The GERG-2004 equation of state

The GERG-2004 equation of state has been developed and recently published (Kunz et al., 2007) as a research project supported by the "Groupe Européen de Recherches Gazières".

Within the natural gas industry, the accurate knowledge of the thermodynamic properties of natural gases and other mixtures of natural gas components is of importance for the basic engineering, performance assessment of existing plants, gas metering, transmission, and storage. Processing, transportation, and storage of natural gas requires property calculations for a wide range of mixture compositions and operating conditions in the homogeneous gas, liquid, and supercritical regions, and also for vapor-liquid equilibrium states. These data can be calculated from equations of state, but either cubic equation of state or other such as the AGA8-DC92 equation of state (used by ISO 12213 "Natural Gas – Calculation of Compression Factor") present weaknesses and limitations.

Most of the standard natural gas applications, such as gas transmission and storage, are located in the "classical" natural gas region, i.e. the gas phase at temperatures from 250 K to 350 K and pressures up to 30 MPa, this range is of main interest for the calculation of thermodynamic properties and is addressed by the new equation.

To be able to reproduce experimental values, for both pure components and mixtures , within experimental errors, the GERG-2004 equation uses a larger number of regressed parameter with respect to cubic equations of state

The GERG-2004 equation of state is explicit in the Helmholtz free energy with density and temperature as independent variables:

$$a(\rho,T) = a^0(\rho,T) + a^r(\rho,T) \tag{6}$$

Usually, the Helmholtz free energy is used in dimensionless form, as $\alpha = a / RT$ and by introducing the adimensional variables $\delta = \rho / \rho_c$ (reduced density) and $\tau = T_c / T$ (reduced temperature) can be written as:

$$\alpha(\delta,\tau) = a^0(\delta,\tau) + a^r(\delta,\tau) \tag{7}$$

It is not possible to describe here in detail how the GERG-2004 equation expands the ideal and residual Helmoltz energy parts by means of a large number of complex polynomial and exponential terms. The level of complexity of the equation can be guessed by noting that it uses up to 110 parameters to define the pure fluid behavior and 89 binary coefficients for each component-component interaction.

These figures are to be compared to 3 pure component parameters and 1 interaction coefficient used by cubic equations of state.

## 5. Calculations, Results and Conclusion

We have considered a LNG re-gasification process, which scope is to feed a high-pressure pipeline distribution system. The liquefied LNG is heated from about -120°C

to about 3-5°C before it is fed to a pipeline for transportation. The pressure at pipeline inlet is assumed to be 60 bar. Taking into account the design pressure of system and the overpressure developed before PSV opening, we can assume 80 bar as relief pressure.
The LNG composition is shown on Table 1

*Table 1 – LNG composition*

| **Component** | **Molar composition, %** |
|---|---|
| Methane | 91.0 |
| Ethane | 4.5 |
| Propane | 3.5 |
| n-Butane | 1.0 |
| Nitrogen | 0.5 |

The phase envelope of this composition is presented on Figure 1, showing that the relief pressure is supercritical. Pressure and temperature values of the critical and other thermodynamic points are shown on Table 2.

*Table 2 – Mixture critical data*

| Point | Temperature, °C | Pressure, bar |
|---|---|---|
| Cricondentherm | -25.279 | 49.7 |
| Cricondenbar | -40.935 | 77.6 |
| Critical point | -58.053 | 67.8 |

The built test case considers a LNG relief at 80 bar with temperatures spanning the range from total liquid, at the inlet at the heating system , to total vapour at the outlet side before entering the pipeline.
Calculations have been performed using the method described above, and an implementation of the GERG-2004 equation in the XPSIM process simulation software for the calculation of enthalpy, entropy, density and heat-capacity.
Since the relief is critical, is it sufficient to compare the calculated sonic velocities. The results obtained are presented on Table 3.
Though the difference in the high temperature region (vapor phase) is quite low, at lower temperatures, nearer to the liquid region the calculated difference is higher approaching 9%.
This difference in the sonic speed value will be reflected either in the calculation of the safety device area or, for a given installed device, in the calculated discharge flow-rate.

*Fig. 1 – LNG phase envelope*

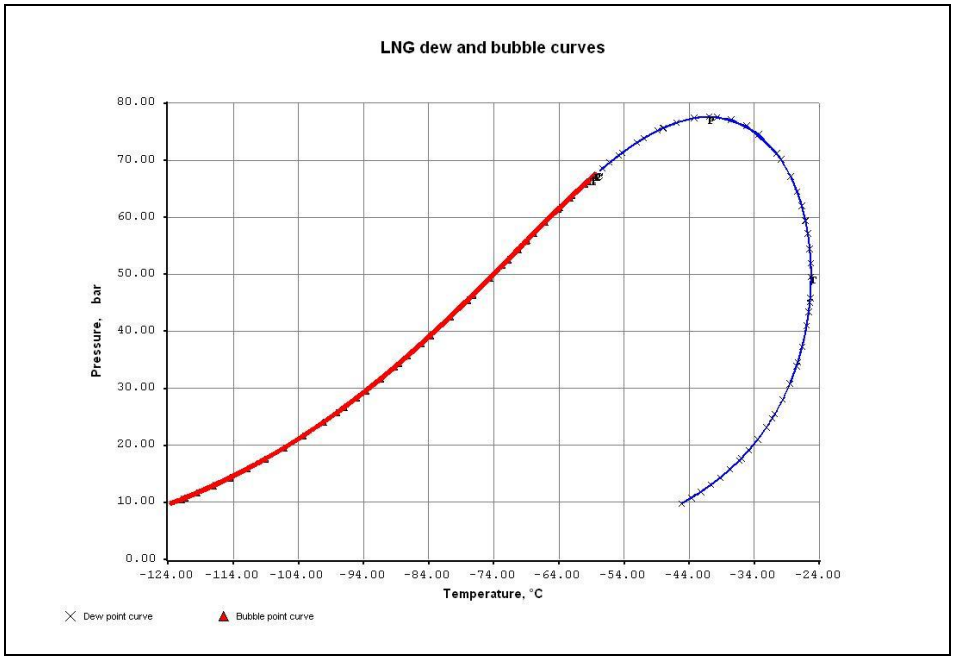


*Table 3 – Sonic velocity comparison – SRK and GERG-2004*

| Relief temp | Crit flow pres | Crit flow temp | Sonic velocity | Crit flow press | Crit flow temp | Sonic velocity | Sonic vel. diff. |
|---|---|---|---|---|---|---|---|
| | SRK | | | GERG-2004 | | | |
| °C | bar | °C | m/s | bar | °C | m/s | % |
| -75 | 41.9 | -81.4 | 175.0 | 43.2 | -80.2 | 172.4 | 1.51 |
| -70 | 47.4 | -76.5 | 155.5 | 48.7 | -75.4 | 151.5 | 2.64 |
| -65 | 53.2 | -71.4 | 146.0 | 54.5 | -70.5 | 136.5 | 6.96 |
| -61 | 58.0 | -67.1 | 133.0 | 58.7 | -66.5 | 129.8 | 2.47 |
| -60 | 56.1 | -68.2 | 143.4 | 58.3 | -66.5 | 131.7 | 8.88 |
| -59 | 55.5 | -68.4 | 148.2 | 56.1 | -67.9 | 139.3 | 6.39 |
| -55 | 52.5 | -69.2 | 167.0 | 52.9 | -69.1 | 160.2 | 4.24 |
| -50 | 50.5 | -68.6 | 190.5 | 50.4 | -68.9 | 186.1 | 2.36 |
| -40 | 48.2 | -63.4 | 232.6 | 48.3 | -63.5 | 230.2 | 1.04 |
| -30 | 47.3 | -55.9 | 261.1 | 47.3 | -55.8 | 259.3 | 0.69 |
| -20 | 46.8 | -48.2 | 281.0 | 47.0 | -47.9 | 279.5 | 0.54 |

Comparisons performed show that calculated differences are almost negligible in the gas phase region but become greater in the two phase region. Though in general cubic equations can be satisfactorily used for engineering design and safety analyses, simulations using the GERG-2004 equation should be considered and applied to assess risk evaluations in some difficult cases.

## 6. References

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