

Article

Critical-Flow Characteristics and Mass-Flux Prediction for High-Pressure Ethylene Relief

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Abstract

High-pressure ethylene relief is a key safety issue in low-density polyethylene production, where ethylene is typically handled under dense real-fluid conditions. Conventional ideal-gas relief equations may lead to significant errors because thermodynamic properties vary strongly with pressure and temperature. In this study, a real-fluid isentropic relief model was developed using thermodynamic properties obtained from the Reference Fluid Thermodynamic and Transport Properties Database (REFPROP). The critical mass flux was determined by searching for the maximum value along the isentropic expansion path, and the equivalence between the maximum-mass-flux condition and the sonic condition was examined. Four industrial relief cases were compared with proprietary design-calculation outputs. The real-fluid model predicted mass flow rates with deviations of -9.9% , -9.1% , -2.3% , and -1.0% , whereas the ideal-gas model produced larger underpredictions, particularly under ultra-high-pressure conditions. The effects of upstream pressure and temperature on critical mass flux, depressurization paths, speed of sound, and critical pressure ratio were analyzed. A response-surface correlation based on 95 calculated states was developed for preliminary estimation, with all deviations within $\pm 10\%$ over the fitted domain. These results demonstrate the importance of accounting for real-fluid thermodynamics when evaluating high-pressure ethylene relief capacity.

Keywords: high-pressure ethylene; critical flow; relief system; real-fluid model; mass flux

1. Introduction

Low-density polyethylene is widely used in packaging, construction, cushioning materials, and other industrial applications because of its flexibility, chemical resistance, and processability [1–4]. Industrial low-density polyethylene production uses ethylene as the main monomer and is typically carried out by free-radical polymerization at pressures of 200–300 MPa and temperatures of 150–300 °C [5–7]. Under such conditions, the process inventory contains a large amount of stored energy. Mechanical failure, blockage, pressure-control malfunction, or other non-reactive overpressure scenarios may cause the rapid release of high-pressure ethylene, resulting in physical explosion hazards, high-momentum jets, flammable vapor clouds, jet fires, or vapor cloud explosions [8,9].

Pressure-relief devices, such as rupture disks, safety valves, and emergency relief systems, are therefore installed at reactors, separators, compressor outlets, and high-pressure pipelines in polyethylene plants. Accurate prediction of the relief mass flux is essential for



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sizing these devices [10]. Existing standards and codes, including American Petroleum Institute Standard 520 (API 520) [11], International Organization for Standardization Standard 4126 (ISO 4126) [12], and the American Society of Mechanical Engineers Boiler and Pressure Vessel Code Section VIII (ASME BPVC Section VIII) [13], provide widely used equations for vapor relief. Their conventional vapor-sizing equations are convenient and well established, but they are generally formulated using ideal-gas or simplified compressible-flow relations, together with empirical discharge coefficients. For high-pressure ethylene, these equations may not reproduce the strong variation in density, enthalpy, isentropic derivative, and sonic velocity along the expansion path [14,15]. Consequently, neither the ideal-gas critical pressure ratio nor the ideal-gas mass-flux equation can reliably describe the relief behavior.

Although proprietary correlations have been developed for high-pressure ethylene relief, publicly available studies of its dense real-fluid critical-flow behavior remain limited. This work develops a real-fluid isentropic model to analyze the critical mass flux, depressurization path, critical speed of sound, and transition between critical and subcritical flow, and proposes an engineering correlation for preliminary mass-flux estimation. Here, “dense real fluid” denotes a single-phase fluid whose high density, intermolecular interactions, and finite molecular volume cause substantial departures from ideal-gas behavior, as reflected by a compressibility factor different from unity and strong state dependence of thermodynamic properties. The term does not imply a liquid phase; ethylene may remain single-phase and supercritical while exhibiting liquid-like density or low compressibility.

The proposed method is a thermodynamic supplement to, rather than a replacement for, code-based relief design. Final device selection must still satisfy applicable code, certified-capacity, discharge coefficient, back pressure, and installation requirements. The objective is to quantify real-fluid effects on the theoretical mass flux and support preliminary evaluation under high-pressure polyethylene-process conditions.

2. Model Development and Case Comparison

2.1. Geometrical Model and Basic Assumptions

The relief process considered in this study is the discharge of single-phase high-pressure ethylene from a large upstream vessel or header through a short relief orifice or short passage to a lower-pressure system, shown in Figure 1. The upstream volume is assumed to be sufficiently large relative to the relief passage such that Section 0–0 can be represented by a stagnation state. The model is based on the following assumptions:

1. The flow through the relief passage is treated as one-dimensional and quasi-steady, with u , ρ , and G interpreted as cross-section-averaged quantities at the effective flow section. This approximation is intended for short, axisymmetric or approximately orifice-like passages with known effective flow area and discharge coefficient. Radial non-uniformity, curved passages, complex valve trims, and local flow separation are not resolved; practical devices with such features require a certified or experimentally determined device-specific discharge coefficient.
2. Heat transfer during passage through the relief opening is neglected. Because the fluid residence time in a short relief passage is small, the heat transferred through the wall is generally much smaller than the enthalpy converted into kinetic energy. The local expansion is therefore approximated as adiabatic.
3. The thermodynamic expansion is approximated as isentropic when calculating the theoretical mass flux. Entropy generation caused by friction, contraction, and local flow separation is not resolved explicitly. These non-ideal effects are represented through the discharge coefficient C_d .
4. Changes in potential energy are neglected because the elevation difference across the short relief passage is negligible relative to the enthalpy and kinetic-energy changes.

5. The fluid is assumed to remain single-phase along the calculated expansion path. Two-phase flashing, delayed phase transition, non-equilibrium nucleation, and chemical decomposition are outside the scope of the present model.

Accordingly, the model is intended for preliminary thermodynamic analysis of single-phase ethylene discharge through a short orifice-like passage with a known effective flow area and an appropriate discharge coefficient. The four industrial cases cover upstream pressures of 39.1–363.93 MPa, temperatures of 100–188.2 °C, and equivalent diameters of 9.8–25 mm. The response-surface correlation is fitted over $P_0 = 20$ –380 MPa and $T_0 = 50$ –250 °C and should be used only within this domain. These ranges are not universal validity limits of the equation of state (EOS); states above 300 MPa or 450 K require extrapolation of the Smukala EOS [16], as discussed in Section 2.7.

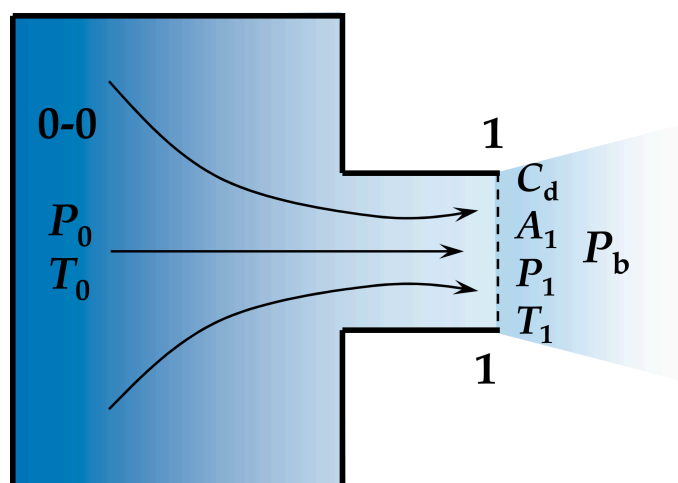


Figure 1. Schematic diagram of high-pressure ethylene relief.

2.2. Real-Fluid Isentropic Relief Model

For a given upstream stagnation state, the steady-flow energy equation between sections 0–0 and 1–1 is

$$h_0 = h_1 + \frac{u_1^2}{2}, \quad (1)$$

and the outlet velocity is

$$u_1 = \sqrt{2(h_0 - h_1)}. \quad (2)$$

Under the isentropic assumption,

$$s_1 = s_0. \quad (3)$$

Therefore, for any trial outlet pressure P_1 , the outlet temperature, enthalpy, and density can be obtained from real-fluid thermodynamic properties along the isentrope:

$$T_1 = T(P_1, s_0). \quad (4)$$

$$h_1 = h(P_1, s_0). \quad (5)$$

$$\rho_1 = \rho(P_1, s_0). \quad (6)$$

The corresponding mass flux is

$$G(P_1) = \rho(P_1, s_0) \sqrt{2[h_0 - h(P_1, s_0)]}. \quad (7)$$

The relief mass flow rate is then

$$q_m = C_d A_1 G. \quad (8)$$

Equation (7) forms the basis of the present real-fluid relief model. Unlike ideal-gas equations, it does not require a constant isentropic exponent or a prescribed critical pressure ratio.

2.3. Determination of Critical Flow and Speed of Sound

For a specified upstream stagnation state (P_0, T_0) , the mass flux at a trial outlet pressure is

$$G(P) = \rho(P, s_0) u(P, s_0). \quad (9)$$

The critical state corresponds to a stationary maximum of the mass flux along the isentrope:

$$\left(\frac{dG}{dP} \right)_{s_0} = 0. \quad (10)$$

Because $G = \rho u$, this condition can be written as

$$\frac{1}{G} \left(\frac{dG}{dP} \right)_{s_0} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_s + \frac{1}{u} \left(\frac{du}{dP} \right)_{s_0} = 0. \quad (11)$$

From the steady-flow energy equation,

$$h_0 = h + \frac{u^2}{2}, \quad (12)$$

differentiation along the isentrope gives

$$u \left(\frac{du}{dP} \right)_{s_0} = - \left(\frac{\partial h}{\partial P} \right)_s. \quad (13)$$

According to the Gibbs relation $dh = T ds + v dP$, at constant entropy,

$$\left(\frac{\partial h}{\partial P} \right)_s = v = \frac{1}{\rho}. \quad (14)$$

Therefore,

$$\left(\frac{du}{dP} \right)_{s_0} = - \frac{1}{\rho u}. \quad (15)$$

Substitution into the stationary-mass-flux condition yields

$$u^2 = \left(\frac{\partial P}{\partial \rho} \right)_s. \quad (16)$$

Since the equilibrium isentropic speed of sound is defined by

$$a^2 = \left(\frac{\partial P}{\partial \rho} \right)_s, \quad (17)$$

the maximum-mass-flux condition gives

$$u_c = a_c, \quad (18)$$

or equivalently,

$$Ma_c = 1. \quad (19)$$

Thus, for the present one-dimensional, single-phase, equilibrium and isentropic model, the maximum of the mass-flux curve is equivalent to the sonic condition. Here, the subscript c denotes the critical state, u is the local velocity, a is the equilibrium speed of sound, and $Ma = u/a$ is the Mach number.

2.4. Comparison with Ideal-Gas Model

For comparison, the ideal-gas critical mass flux G_{ig} is calculated as [11–13]:

$$G_{ig} = P_0 \sqrt{\frac{k}{R_g T_0} \left(\frac{2}{k+1} \right)^{\frac{k+1}{k-1}}}. \quad (20)$$

Here, R_g is the specific gas constant and k is the isentropic exponent. In conventional engineering use of the ideal-gas critical-flow equation, $k = c_p/c_v$ is generally evaluated at the upstream relieving state and then treated as constant during the idealized isentropic expansion. This upstream-state convention is adopted here so that Equation (20) remains consistent with its standard algebraic derivation. An effective or path-averaged value of k may sometimes be used as an engineering approximation when heat capacities vary, but the resulting value depends on the selected averaging definition and expansion interval. More importantly, averaging k does not reproduce the coupled real-fluid variation in enthalpy, density, and speed of sound. Equation (20) is therefore used only as an ideal-gas benchmark and not as the recommended design equation for high-pressure ethylene. In the following ideal-gas calculation, k was evaluated at the upstream pressure and temperature using the REFPROP database.

2.5. Calculation Procedure

The calculation procedure is shown in Figure 2. For each upstream state defined by P_0 and T_0 , the stagnation enthalpy h_0 and entropy s_0 are first obtained from REFPROP 10. The outlet pressure P_1 is then varied along the isentropic line. At each pressure point, REFPROP is used to calculate $T(P_1, s_0)$, $h(P_1, s_0)$, $\rho(P_1, s_0)$, and the local speed of sound. The velocity and mass flux are subsequently obtained from Equations (2) and (7), respectively. The critical state is identified by the maximum mass flux, with $Ma \approx 1$ used as a consistency check. Finally, the relief mass flow rate is calculated using $\dot{q}_m = C_d A_1 G_c$.

The thermodynamic properties of ethylene are calculated using REFPROP with the EOS developed by Smukala et al. [16].

2.6. Case Comparison with Industrial Design Data

Four ethylene relief cases were used to assess the present model against data from an Engineers and Constructors International, Inc. (ECI) process-design package, as listed in Table 1. The ECI values are proprietary design-calculation outputs rather than laboratory or plant measurements; the underlying property method, calculation procedure, and empirical corrections were unavailable. They are therefore treated as an external industrial engineering benchmark rather than experimental validation data.

The cases cover initial pressures of 39.1–363.93 MPa, initial temperatures of 100–188.2 °C, relief diameters of 9.8–25 mm, and a discharge coefficient of $C_d = 0.7$. Cases 1 and 2 exceed the nominal upper-temperature limit of the Smukala EOS [16] by 11.35 and 9.92 K, respectively. Case 3 exceeds the nominal upper-pressure limit by 63.93 MPa, corresponding to approximately 21.3% of the stated upper limit. Case 4 lies within the nominal EOS range. Consequently, Case 4 provides the strongest within-range engineering comparison, whereas Cases 1–3 should be interpreted as extrapolative industrial comparisons. Their

agreement with the ECI data does not by itself establish thermodynamic accuracy outside the validated EOS range.

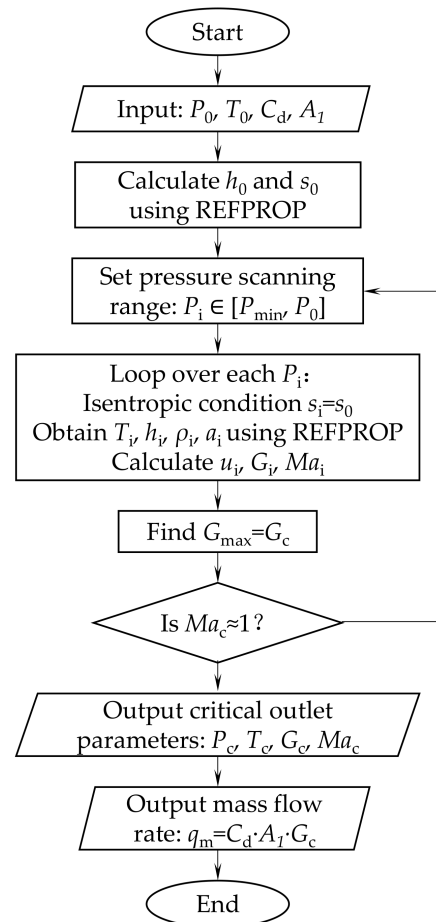


Figure 2. Calculation procedure for critical mass flux based on REFPROP.

Table 1. Comparison of case-study results calculated using different methods.

Item	Variables	Case 1	Case 2	Case 3	Case 4
Initial conditions	Initial pressure P_0 (MPa)	39.1	41.697	363.93	169.5
	Initial temperature T_0 (°C)	188.2	186.77	100	100
	Relief diameter d (mm)	9.8	25	15	15
	Discharge coefficient C_d	0.7	0.7	0.7	0.7
ECI results *	Outlet pressure P_1 (MPa)	13.38	13.77	42.56	21.51
	Outlet temperature T_1 (°C)	114.7	112.4	12.1	27.3
	Mass flow rate $\dot{q}_m$ (kg·s ^{−1})	4.76	32.90	64.74	39.97
Real-fluid model results	Outlet pressure P_1 (MPa)	18.88	19.69	49.98	27.33
	Outlet temperature T_1 (°C)	139	137	16	32
	Mass flow rate $\dot{q}_m$ (kg·s ^{−1})	4.29	29.89	63.23	39.57
Ideal-gas model results	Mass flow rate $\dot{q}_m$ (kg·s ^{−1})	4.01	27.49	40.30	26.02

* ECI values are design-calculation outputs extracted from an industrial process package. They are not experimental measurements. The proprietary calculation method was unavailable to the authors.

A common discharge coefficient of $C_d = 0.7$ was specified in the industrial process-package data for the four cases and was retained in the present comparison. The real-fluid model predicts the theoretical critical mass flux independently of passage diameter; diameter and discharge coefficient enter only when converting the mass flux into the

mass flow rate through $q_m = C_d A_1 G_c$. The use of the same C_d for the four diameters is therefore a feature of the available engineering dataset rather than a general conclusion of the present study. In practice, C_d may depend on relief-device geometry, Reynolds number, pressure ratio, orifice thickness, roughness, flow separation, and valve opening characteristics. Device-specific certified or experimentally determined values should be used in final sizing calculations.

The predicted critical outlet pressures and temperatures follow the trends of the ECI values, although quantitative differences remain, particularly in the outlet pressures of Cases 1 and 2. Agreement in outlet temperature is closer for the two higher-pressure cases.

Figure 3 compares the mass flow rates, which are the quantities most relevant to relief sizing. Deviations of the real-fluid model from the ECI values are -9.9% , -9.1% , -2.3% , and -1.0% for Cases 1–4, respectively, compared with ideal-gas underpredictions of 15.8% , 16.4% , 37.8% , and 34.9% . The ideal-gas discrepancy is therefore particularly large under ultra-high-pressure conditions.

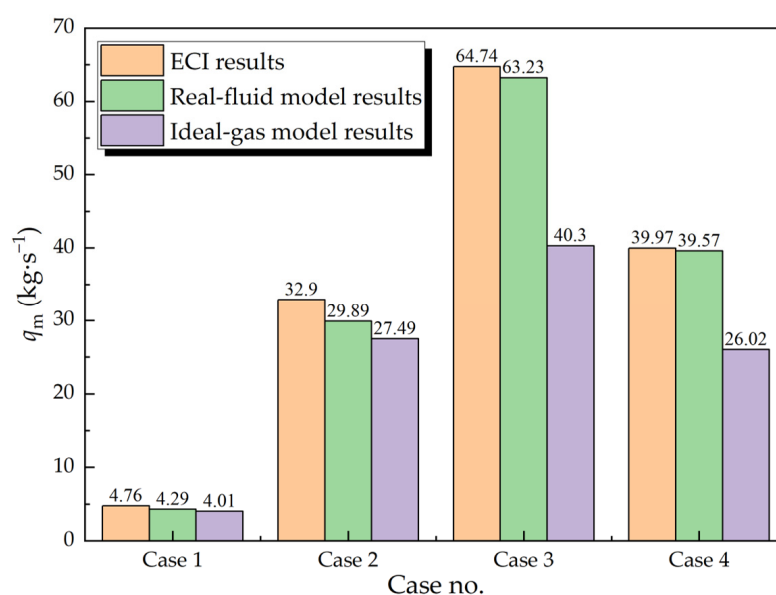


Figure 3. Direct comparison of the mass flow rates obtained from the ECI industrial design calculations, the present real-fluid model, and the ideal-gas model for Cases 1–4.

The underprediction by the ideal-gas model is mainly caused by its assumptions of constant isentropic exponent, fixed critical pressure ratio, and temperature-dependent speed of sound. These assumptions cannot represent the strong pressure and temperature dependence of density, compressibility, enthalpy, entropy, and speed of sound in high-pressure ethylene. Although the present real-fluid model still differs from the proprietary ECI method because of possible differences in empirical corrections, property methods, and equipment effects, it provides a much closer prediction of relief capacity than the ideal-gas model. The model is therefore considered suitable for analyzing high-pressure ethylene relief behavior and for developing engineering mass-flux correlations.

2.7. Assessment of EOS Extrapolation and Thermodynamic Sensitivity

REFPROP calculations were based on the Smukala et al. EOS [16], whose stated range extends from the melting line to 450 K and up to 300 MPa. As quantified in Section 2.6, Cases 1–3 partly exceed this range, whereas Case 4 remains within it. The following analysis therefore evaluates the available external property agreement and the sensitivity of mass flux to representative property discrepancies.

Independent experimental property data covering all extrapolated states were unavailable. In addition, the detailed property method used in the proprietary ECI process package was not disclosed. As a limited external benchmark, Table 2 compares densities calculated using the Smukala EOS with the densities reported in the ECI package at four representative high-pressure or high-temperature states. The relative difference was calculated as

$$\delta_{\rho} = \frac{\rho_{\text{Smukala}} - \rho_{\text{ECI}}}{\rho_{\text{ECI}}} \times 100\%. \quad (21)$$

The absolute relative density differences range from 0.83% to 3.94%. The smaller differences occur at the high-temperature states near 35–43 MPa, whereas differences of approximately 3.6–3.9% occur at the ultra-high-pressure states. Because the ECI values are proprietary property-calculation outputs rather than experimental measurements, these differences should be interpreted as an external model-form benchmark and not as the true error of the Smukala EOS.

The propagation of thermodynamic-property discrepancies into the mass flux can be assessed from

$$G = \rho \sqrt{2(h_0 - h_1)} = \rho \sqrt{2\Delta h}. \quad (22)$$

Taking the logarithmic differential gives

$$\frac{dG}{G} = \frac{d\rho}{\rho} + \frac{1}{2} \frac{d(\Delta h)}{\Delta h}. \quad (23)$$

Therefore, the local logarithmic sensitivity coefficients are

$$S_{\rho} = \frac{\partial \ln G}{\partial \ln \rho} = 1. \quad (24)$$

$$S_{\Delta h} = \frac{\partial \ln G}{\partial \ln \Delta h} = \frac{1}{2}. \quad (25)$$

Using the maximum density discrepancy in Table 2, 3.94%, as a representative perturbation, the corresponding first-order change in mass flux is approximately 3.94% if the enthalpy drop is held fixed. An equal relative perturbation in Δh produces an approximately 1.97% change in G . If both quantities are perturbed by 3.94% in the same direction, the first-order combined change is approximately 5.91%. These values provide a basic sensitivity bound and do not constitute a substitute for experimental EOS validation, because density and enthalpy are thermodynamically coupled in the actual EOS calculation.

The industrial comparisons, particularly the within-range result for Case 4, support the engineering usefulness of the formulation. However, Cases 1–3 remain conditional on EOS extrapolation and should not be interpreted as high-accuracy thermodynamic validation. Reducing this uncertainty would require additional high-pressure measurements or comparisons with independently validated EOS formulations.

Table 2. Comparison of ethylene densities calculated using the Smukala EOS with property values reported in the ECI process package at representative states.

<i>P</i> (MPa)	<i>T</i> (°C)	ρ_{ECI} (kg·m ^{−3}) *	ρ_{Smukala} (kg·m ^{−3})	Relative Difference (%)
42.9828	194.4	291.4602	293.89	0.83
35.1624	181.3	268.8172	271.11	0.85
400.036	106.0	600.2401	623.87	3.94
327.3004	93.6	584.4535	605.67	3.63

* The ECI values are proprietary property-calculation outputs rather than experimental measurements; therefore, the tabulated differences represent an external model-form benchmark.

3. Results and Discussion

3.1. Variation in Relief Mass Flux and Development of Correlation

Figure 4 shows the variation in the critical mass flux G_c with upstream stagnation pressure P_0 at different stagnation temperatures T_0 . Within the investigated range, G_c increases monotonically with P_0 , but the growth rate decreases at higher pressures. This nonlinear behavior reflects the dense-fluid properties of high-pressure ethylene. At the critical section, $u_c = a_c$ and therefore $G_c = \rho_c a_c$. Increasing P_0 generally increases both the critical density and the speed of sound, leading to a higher mass flux. However, in the high-pressure dense-fluid region, the relative increases in density and speed of sound become smaller, and the marginal increase in G_c gradually weakens.

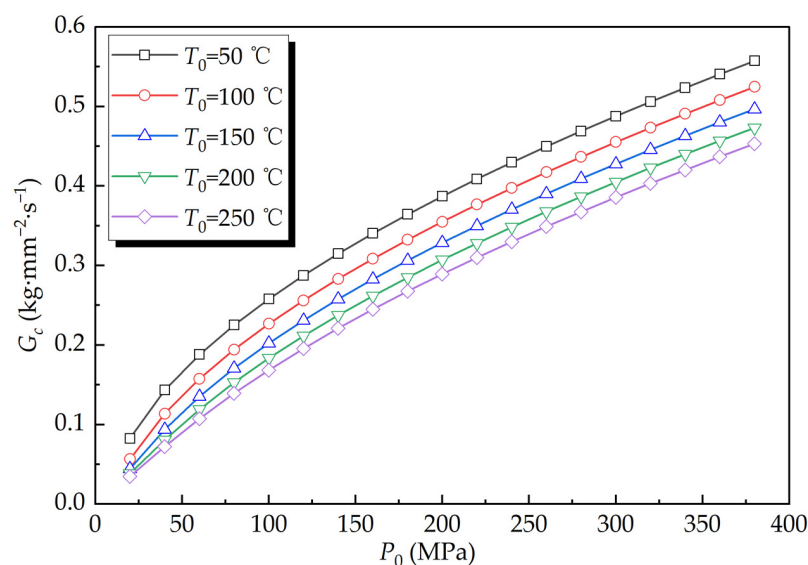


Figure 4. REFPROP-based critical mass flux G_c as a function of upstream stagnation pressure P_0 at different upstream stagnation temperatures T_0 . The critical state is defined by the maximum of $G(P_1)$ along the isentropic expansion path, corresponding to $Ma = 1$.

The upstream temperature also affects the critical mass flux. At the same P_0 , a higher T_0 usually gives a lower G_c because the density at the critical section decreases. Although temperature may increase the speed of sound in low-pressure gas-like regions, the reduction in density dominates the mass-flux behavior over most of the conditions studied. The temperature effect is coupled with pressure: it is more pronounced in the lower-pressure region and becomes less straightforward in the dense supercritical region, where density, compressibility, enthalpy drop, and speed of sound are strongly coupled.

A numerical dataset was generated from the real-fluid model over $P_0 = 20$ –380 MPa and $T_0 = 50$ –250 °C. Pressure was sampled at 20 MPa intervals, giving 19 pressure levels, and temperature was sampled at 50 °C intervals, giving five temperature levels. The complete structured grid therefore contained $N = 95$ upstream thermodynamic states. For each state, the outlet pressure was varied along the corresponding isentrope, and G_c was determined from the maximum of the mass-flux curve. All 95 calculated states were used to determine the final coefficients by ordinary least-squares regression. The resulting correlation should be regarded as a reduced-order surrogate of the REFPROP-based real-fluid model rather than as an independent experimental correlation. The ECI industrial cases were not used in determining the response-surface coefficients.

The dimensionless variables were defined as

$$x = \ln \frac{P_0}{P_{\text{ref}}}, \quad (26)$$

$$\theta = \frac{T_0 - T_{\text{ref}}}{T_{\text{scale}}}, \quad (27)$$

and

$$y = \ln\left(\frac{G_c}{G_{\text{ref}}}\right). \quad (28)$$

The response surface was expressed as

$$y = b_1 + b_2x + b_3x^2 + b_4\theta + b_5\theta^2 + b_6x\theta. \quad (29)$$

Here, $P_{\text{ref}} = 100$ MPa, $T_{\text{ref}} = 150$ °C, $T_{\text{scale}} = 100$ °C, and $G_{\text{ref}} = 1$ kg·mm^{−2}·s^{−1}. The fitted coefficients are $b_1 = -1.6009$, $b_2 = 0.7590$, $b_3 = -0.0757$, $b_4 = -0.2278$, $b_5 = 0.0325$, and $b_6 = 0.1063$. Because the regression is formulated in terms of the dimensionless ratio G_c/G_{ref} , G_c and G_{ref} must be expressed in the same units. In this study, both are expressed in kg·mm^{−2}·s^{−1}.

Figure 5 compares the mass fluxes calculated by the real-fluid model with those predicted by the response-surface correlation. Most data points are close to the diagonal line, indicating that the response-surface model captures the dependence of G_c on P_0 and T_0 . The relative deviation is defined as

$$\varepsilon_i = \frac{G_{\text{corr},i} - G_{\text{RF},i}}{G_{\text{RF},i}} \times 100\%, \quad (30)$$

where $G_{\text{corr},i}$ and $G_{\text{RF},i}$ are the correlation and REFPROP-based values, respectively; positive deviations indicate overprediction. Figures 5 and 6 show that the correlation reproduces the calculated data well, with all deviations within $\pm 10\%$ and a mean relative deviation of 1.376%. The largest deviations occur at 20 MPa because these states lie at the lower boundary of the fitted domain, where the transition toward gas-like behavior is represented by a single global second-order surface with only one-sided neighboring data. Moreover, the lower mass flux at 20 MPa converts a similar absolute residual into a larger relative deviation. This is therefore a fitting effect rather than a discontinuity in the REFPROP calculation. The correlation is suitable for preliminary sizing and parametric analysis only within the fitted domain.

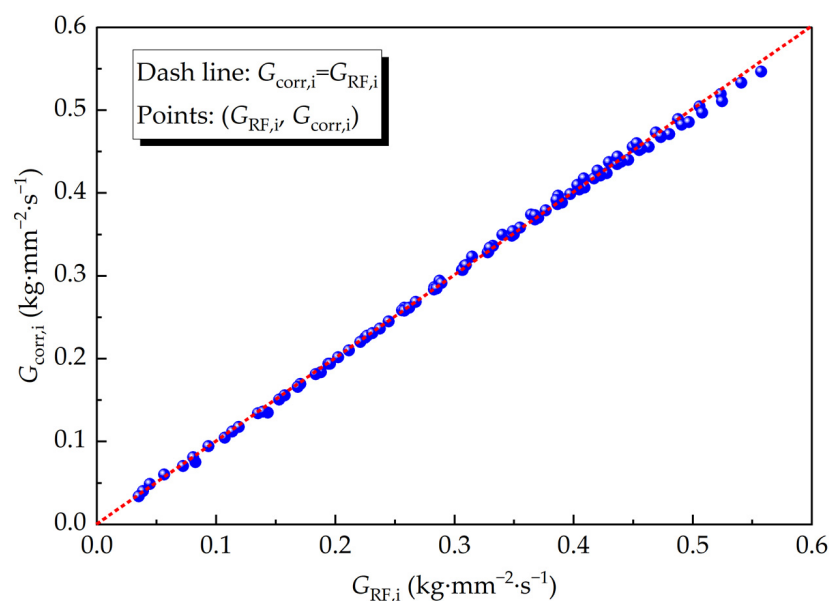


Figure 5. Comparison between the critical mass flux calculated using the real-fluid model and that predicted by the response-surface correlation. Symbols represent individual calculated thermodynamic states, and the solid diagonal line represents exact agreement, $G_{\text{corr},i} = G_{\text{RF},i}$.

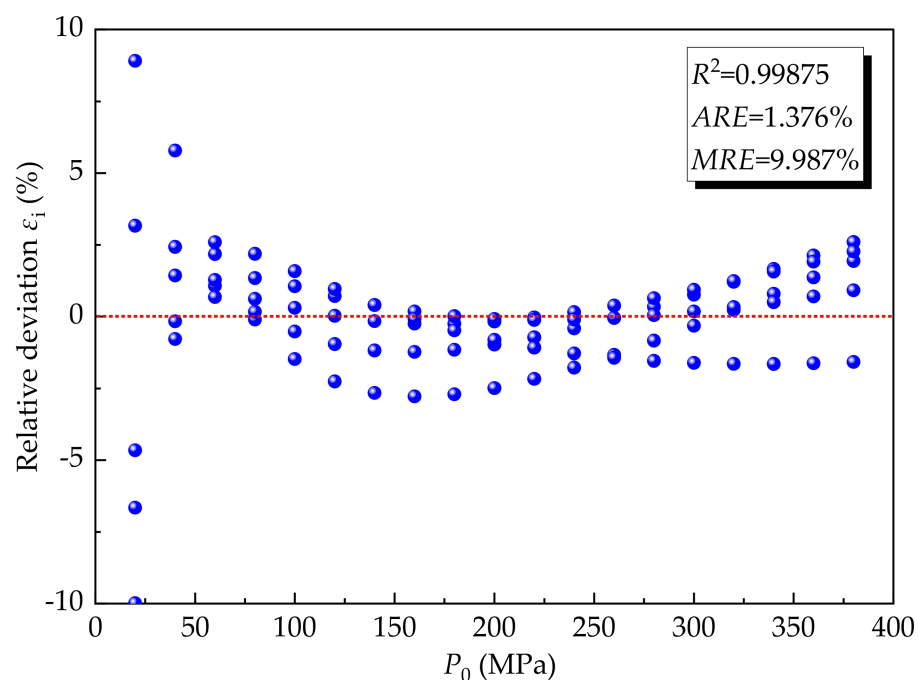


Figure 6. Relative deviation of the response-surface prediction from the REFPROP-based critical mass flux at different upstream pressures and temperatures. Positive values indicate overprediction by the correlation, and negative values indicate underprediction.

3.2. Isentropic Depressurization Path and Real-Fluid Effects

Nine representative cases were selected to separate the effects of upstream pressure and temperature. Cases A–D use a fixed upstream pressure of 380 MPa with temperatures from 100 to 250 °C, whereas Cases E–I use a fixed upstream pressure of 20 MPa with temperatures from 50 to 250 °C. The former group represents ultra-high-pressure dense-fluid states, while the latter group spans states that become progressively more gas-like as temperature increases. The upstream and calculated critical states are summarized in Table 3.

Table 3. Upstream and critical states for the nine representative depressurization cases.

Case	P_0 (MPa)	T_0 (°C)	s_0 (kJ·kg ^{−1} ·K ^{−1})	Z_0	P_c (MPa)	T_c (°C)
A	380	100	1.0214	5.5400	52	14.7
B	380	150	1.3291	5.0399	72.5	66.2
C	380	200	1.6162	4.6433	89	117.8
D	380	250	1.8868	4.3209	102.3	169.3
E	20	50	1.5493	0.5872	6.25	15.6
F	20	100	1.9991	0.6863	9.8	57.3
G	20	150	2.3766	0.8004	10.8	104.1
H	20	200	2.6885	0.8835	11.1	153.6
I	20	250	2.9619	0.9391	11.3	203.8

Figure 7 presents the isentropic depressurization paths of high-pressure ethylene under different initial conditions. During relief through a short orifice or pipe, part of the stagnation enthalpy is converted into kinetic energy, and the fluid temperature decreases as pressure decreases. The critical state is reached when the mass flux reaches its maximum along the isentropic path.

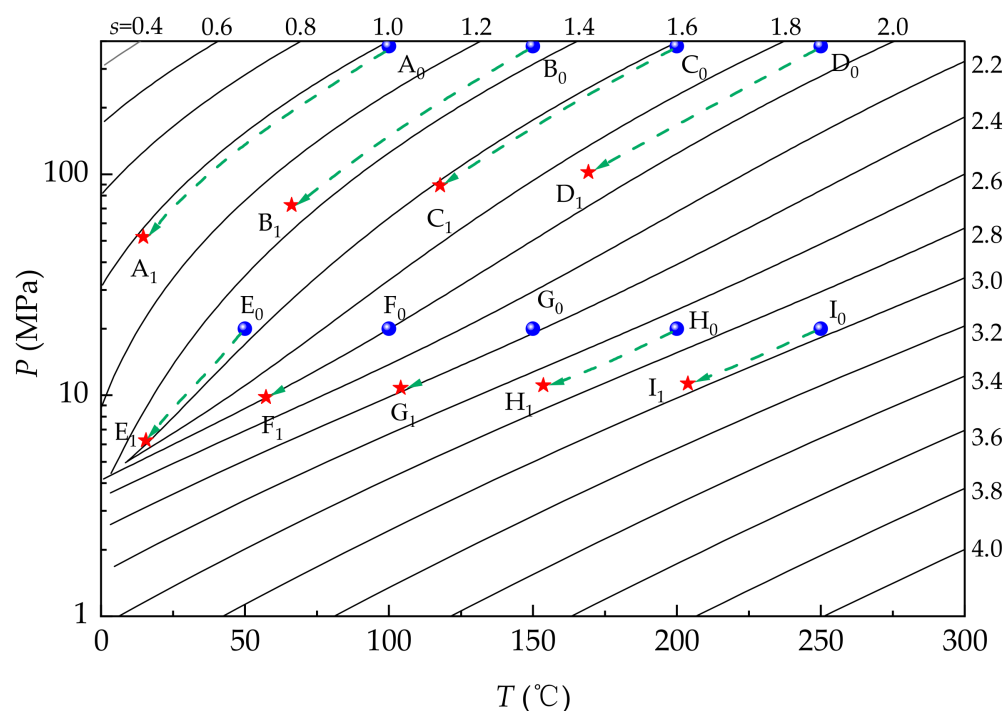


Figure 7. Isentropic depressurization paths (dashed line with arrow) of high-pressure ethylene for Cases A–I in the temperature–pressure plane. The starting ball point of each curve represents the upstream stagnation state, and the terminal star symbol represents the calculated critical state at which G reaches its maximum and $Ma = 1$.

Figure 8 provides a complementary thermodynamic representation of the same cases. Because entropy remains constant in the present model, each expansion path appears as a vertical line in the T – s plane. The intersections with the selected isobars show the progressive reduction in pressure and temperature from the upstream state to the critical state. The markedly different spacing and slopes of the isobars across the investigated entropy and temperature ranges indicate that a given pressure reduction does not produce a universal temperature response. This is consistent with the strong state dependence of the real-fluid thermodynamic derivatives. The upstream compressibility factors listed in Table 3 range from approximately 0.59 to 5.54. The lower-pressure, higher-temperature cases approach gas-like behavior as Z_0 approaches unity, whereas the ultra-high-pressure cases exhibit very large departures from the ideal-gas relation. Thus, although compressibility-factor contours are not superimposed on Figure 8, the combined information from the T – s diagram, the isobars, and Table 3 provides the requested thermodynamic context.

Figures 7 and 8 show that the real-fluid isentropic paths and their critical terminal states are not geometrically similar and cannot be represented by a universal constant- k power law. In the lower-pressure cases, ethylene becomes more gas-like and undergoes a relatively large temperature decrease during expansion. At higher pressures and lower temperatures, compressibility factor, heat capacities, Joule–Thomson coefficient, density, enthalpy, and speed of sound vary strongly with state, producing distinct path curvature and critical states.

Consequently, the critical pressure ratio depends on both upstream pressure and temperature. An ideal-gas critical pressure ratio may therefore introduce substantial errors in the predicted critical pressure, temperature, density, and mass flux; the critical state should instead be obtained from the real-fluid isentropic mass-flux curve.

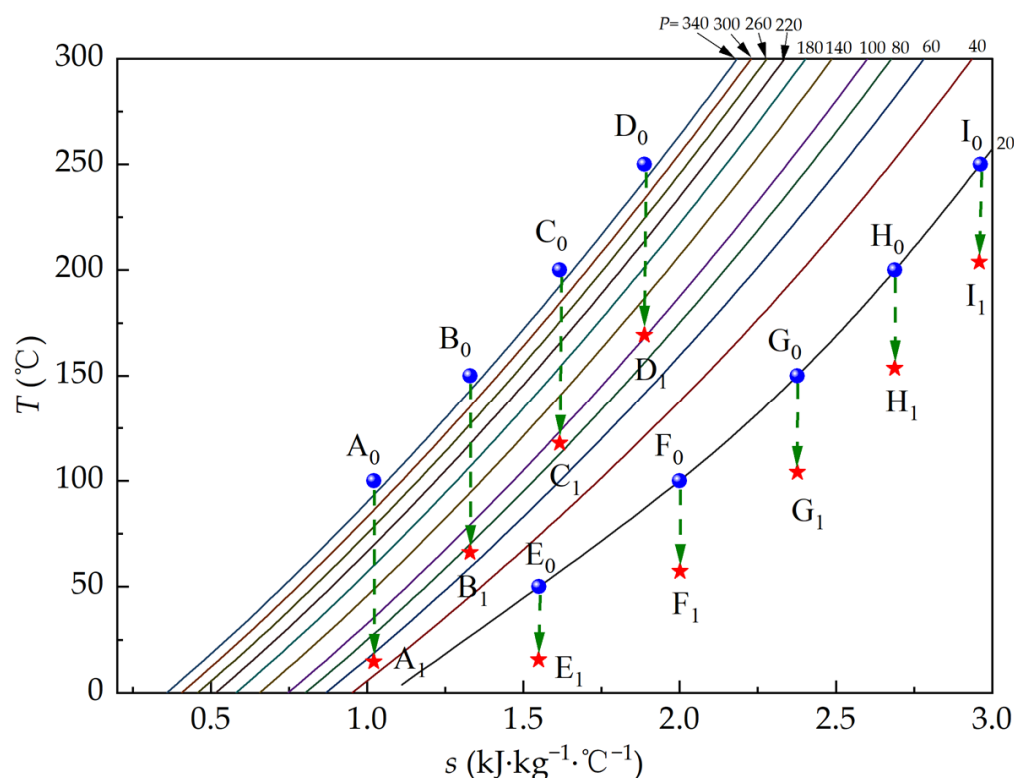


Figure 8. Temperature–entropy diagram depressurization paths (dashed line with arrow) for the investigated high-pressure ethylene relief conditions. The starting ball point of each curve represents the upstream stagnation state, the terminal star symbol represents the calculated critical state at which G reaches its maximum and $Ma = 1$, and the background curves represent selected isobars.

3.3. Critical Outlet Speed of Sound and Dense-Fluid Characteristics

The defining feature of critical flow is that the local velocity reaches the equilibrium speed of sound at the critical section, i.e., $u_c = a_c$ and $Ma_c = 1$. Consequently, $G_c = \rho_c u_c = \rho_c a_c$. For a specified equilibrium thermodynamic model, the speed of sound is uniquely determined by the local state:

$$a^2 = \left(\frac{\partial P}{\partial \rho} \right)_s = \frac{K_s}{\rho}. \quad (31)$$

where $K_s = \rho(\partial P / \partial \rho)_s$ is the isentropic bulk modulus. Density, isentropic compressibility, and bulk modulus are therefore thermodynamically related descriptions of the same local response rather than independent controlling variables.

Figure 9 shows the equilibrium speed of sound at the critical state as a function of upstream pressure and temperature. In the low-pressure gas-like limit, the behavior approaches $a = (kR_g T)^{1/2}$, and temperature is the dominant state variable. In dense high-pressure ethylene, however, $(\partial P / \partial \rho)_s$ varies strongly with state. Increasing pressure generally reduces compressibility and increases the isentropic bulk modulus, thereby increasing the critical-state speed of sound.

At a given high pressure, a lower temperature may produce a higher speed of sound because of the associated higher density and lower compressibility, opposite to the ideal-gas trend. The pressure-induced increases in both ρ_c and a_c raise the critical mass flux, although their relative growth rates diminish at very high pressures. These state-dependent effects explain why ideal-gas equations cannot reliably predict high-pressure ethylene relief.

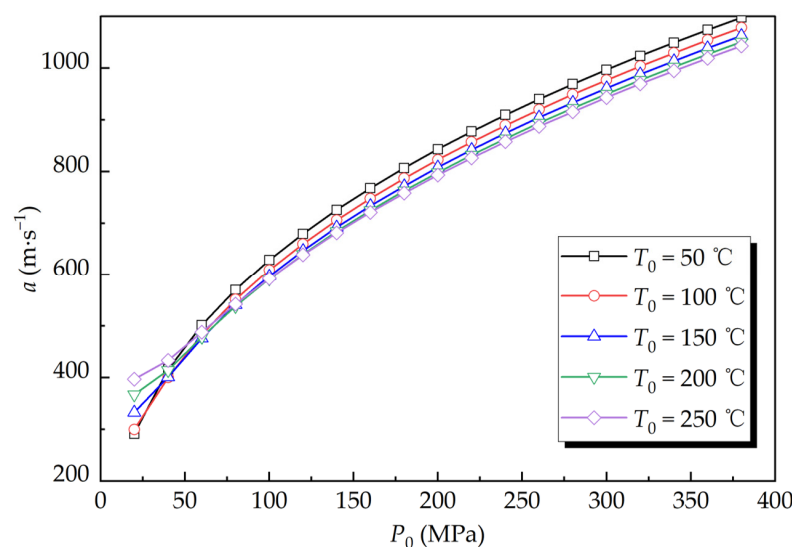


Figure 9. Equilibrium speed of sound at the critical outlet state as a function of upstream stagnation pressure at different upstream temperatures.

3.4. Determination of Critical and Subcritical Flow

The previous sections focused on critical flow. In practical relief systems, however, the flow may become subcritical if the downstream back pressure is sufficiently high [17,18]. For ideal gases, the transition is usually determined using a fixed critical pressure ratio. For high-pressure ethylene, this approach is not applicable because the isentropic exponent and thermodynamic properties vary strongly with pressure and temperature. The critical pressure ratio must therefore be obtained from the real-fluid isentropic mass-flux curve.

For a given upstream stagnation state, the critical pressure ratio is defined as $\beta_c = P_c/P_0$. If the downstream back pressure satisfies $P_b \leq P_c$, the flow is choked, and the mass flux is equal to the critical value G_c . If $P_b > P_c$, the flow is subcritical, the outlet pressure is controlled by the back pressure, and the mass flux should be calculated as $G(P_b)$ along the same isentropic path. Equivalently, critical flow occurs when $P_b/P_0 \leq \beta_c$, whereas subcritical flow occurs when $P_b/P_0 > \beta_c$.

Table 4 lists the critical pressure ratios for the four representative cases. For Cases 1 and 2, with upstream pressures near 40 MPa, β_c is approximately 0.47–0.48. For Cases 3 and 4, with much higher upstream pressures, β_c decreases to 0.137 and 0.161, respectively. This indicates that, under ultra-high-pressure conditions, ethylene relief may remain choked even when the downstream pressure is several tens of megapascals. The results confirm that the critical pressure ratio is not a constant and cannot be represented by the ideal-gas expression.

Table 4. Critical pressure ratio and back-pressure range for subcritical flow.

Case	P_0 (MPa)	T_0 (°C)	P_c (MPa)	$\beta_c = P_c/P_0$	P_b Ranges for Subcritical Flow (MPa)
1	39.1	188.2	18.88	0.483	$18.88 < P_b < 39.1$
2	41.697	186.77	19.69	0.472	$19.69 < P_b < 41.697$
3	363.93	100	49.98	0.137	$49.98 < P_b < 363.93$
4	169.5	100	27.33	0.161	$27.33 < P_b < 169.5$

Figure 10 shows the variation in β_c with P_0 at different T_0 . The region below each curve corresponds to critical flow, whereas the region above each curve corresponds to subcritical flow. Figure 11 presents the same criterion in terms of the critical back pressure

P_c . For any given P_0 and T_0 , critical flow occurs when the actual back pressure is below the corresponding P_c curve; otherwise, the flow is subcritical. These diagrams can be used to determine whether the relief flow is choked for a specified upstream state and downstream pressure before calculating the relief load.

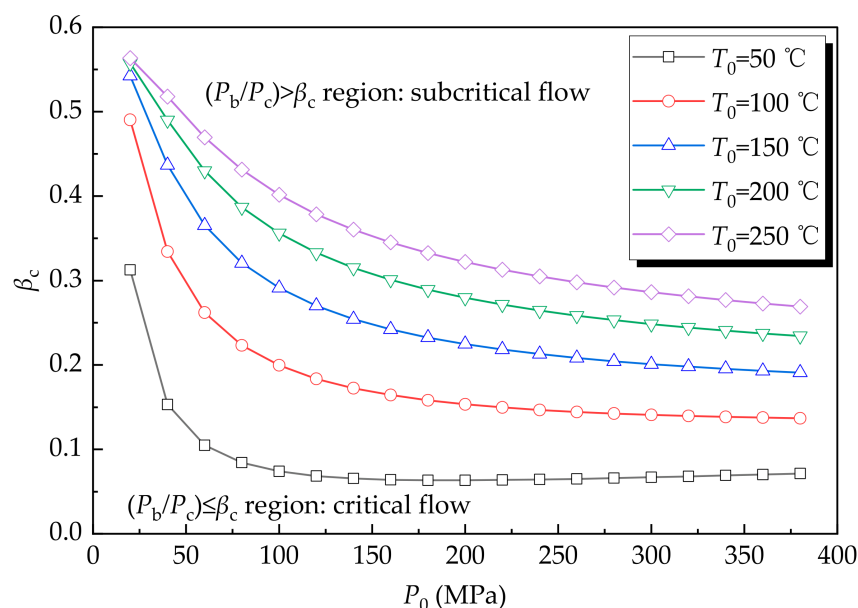


Figure 10. Real-fluid critical pressure ratio $\beta_c = P_c/P_0$ as a function of upstream stagnation pressure at different upstream temperatures. For a specified upstream state, critical flow occurs when $P_b/P_0 \leq \beta_c$, whereas subcritical flow occurs when $P_b/P_0 > \beta_c$.

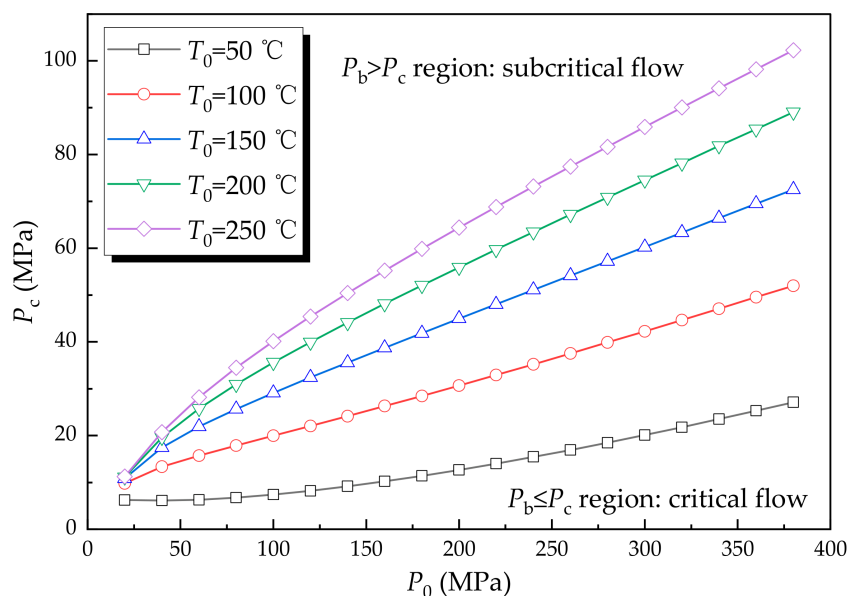


Figure 11. Flow-regime map for high-pressure ethylene relief based on the critical back pressure P_c . Each curve corresponds to a specified upstream temperature. Operating points below the corresponding P_c curve are critical, whereas points above the curve are subcritical.

The 50 °C curve exhibits stronger curvature than the higher-temperature curves. Ethylene has a critical temperature of approximately 9.2 °C; therefore, the 50 °C isotherm is thermodynamically closer to the critical region than the other investigated isotherms. As pressure changes, states on this isotherm can approach or cross a supercritical pseudocritical region characterized by rapid but continuous variations in density, compressibility, heat

capacity, and the isentropic pressure–density derivative. Because P_c is determined by the coupled variation in enthalpy, density, and speed of sound along the isentrope, these property gradients produce the observed nonlinear curvature. The observed curvature reflects continuous property variations in the single-phase supercritical region and does not indicate a phase transition in the calculated states.

4. Conclusions

A real-fluid isentropic model was developed to predict high-pressure ethylene relief under conditions relevant to polyethylene production. The main conclusions are as follows:

(1) The critical state of high-pressure ethylene can be determined from the maximum of the isentropic mass-flux curve, which is consistent with the sonic condition $Ma = 1$.

(2) Compared with the ideal-gas method, the real-fluid model gives substantially closer agreement with the available industrial design-calculation data. The deviations of the real-fluid model are from -9.9% to -1.0% , whereas the ideal-gas model underpredicts the mass flow rates by $15.8\text{--}37.8\%$. These comparisons constitute an engineering benchmark rather than experimental validation, and the results for Cases 1–3 remain conditional on partial EOS extrapolation.

(3) The critical mass flux increases with upstream pressure, but the increasing rate gradually decreases in the dense-fluid region. Higher upstream temperature generally reduces the mass flux because of the decrease in critical density.

(4) The critical pressure ratio of high-pressure ethylene is not constant. It varies strongly with upstream pressure and temperature, so the transition between critical and subcritical flow should be evaluated using real-fluid properties.

(5) A response-surface correlation was developed from 95 REFPROP-based states over $P_0 = 20\text{--}380$ MPa and $T_0 = 50\text{--}250$ °C. All fitting deviations remain within $\pm 10\%$, supporting its use for preliminary estimation within this domain; extrapolation is not recommended.

(6) The present method is restricted to single-phase, equilibrium, quasi-steady discharge through a short relief passage. It does not account explicitly for two-phase flashing, delayed nucleation, slip between phases, thermal non-equilibrium, polymer or solid entrainment, ethylene decomposition, long-pipe friction, or transient depletion of the upstream vessel.

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Abbreviations

The following abbreviations are used in this manuscript:

API	American Petroleum Institute
ISO	International Organization for Standardization
ASME	American Society of Mechanical Engineers
BPVC	Boiler and Pressure Vessel Code
EOS	Equation of state
NIST	National Institute of Standards and Technology
REFPROP	Reference Fluid Thermodynamic and Transport Properties Database
ECI	Engineers and Constructors International, Inc.

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