

Article

Transient Pressure-Relief Characteristics of Ethylene/Vinyl Acetate Mixtures in the High-Pressure Polyethylene Process

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Abstract

Pressure relief in high-pressure polyethylene processes involves dense, strongly non-ideal ethylene-based fluids. A transient real-fluid model was developed for the single-phase discharge of ethylene/vinyl acetate (VA) mixtures by coupling adiabatic vessel depressurization with quasi-steady isentropic nozzle flow. Thermodynamic properties were calculated using the Peng–Robinson equation of state in REFPROP. The admissible mass flux was maximized over single-phase throat states, and sonic choking was verified using $u_1/a_1 \approx 1$. For the validation case at 2000 bar and 25 °C, the calculated pressure history yielded an RMSE of 120 bar, an MAE of 97 bar, and $R^2 = 0.93$. Increasing the VA mass fraction from 0 to 40% increased the initial mass flux from 0.35 to 0.41 kg·mm⁻²·s⁻¹ and shortened the single-phase duration from 761 to 413 ms. Higher initial pressure increased the mass flux, whereas higher initial temperature reduced it and prolonged discharge. The discharge coefficient affected the time scale but not the vessel isentrope or terminal state. Sonic choking occurred during the high-pressure stage, while the flux maximum became phase-boundary-limited near termination. The results represent comparative single-phase trends because two-phase discharge is excluded and the ethylene/VA interaction parameter remains uncertain.

Keywords: ethylene/vinyl acetate mixture; pressure relief; real-fluid flow; transient depressurization; critical mass flux; Peng–Robinson equation of state

1. Introduction

Low-density polyethylene and ethylene/vinyl acetate (VA) copolymers are widely used in flexible packaging, films, adhesives and cable insulation [1,2]. They are produced by free-radical polymerization at pressures of approximately 1000–3000 bar and temperatures of 150–300 °C in tubular or autoclave reactors [3,4]. VA contents may reach approximately 40 mass%, adding a reactive component to an already demanding high-pressure process [5]. Because polymerization is strongly exothermic and the monomer mixture is handled as a dense supercritical or compressed fluid, process safety depends on preventing runaway polymerization and ethylene decomposition and on providing adequate emergency pressure relief [6,7].

Ethylene may decompose violently into carbon, hydrogen and methane when its pressure and temperature exceed the decomposition boundary [5–7]. Reported initiating mechanisms include adiabatic compression during rapid pressurization or

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repressurization, local hot spots caused by fouling or excess initiator, and decomposition fronts propagating through the reactor. VA alters the thermodynamic properties and phase behavior of the reacting mixture and may therefore also affect its emergency discharge characteristics.

Relief sizing under these conditions is thermodynamically challenging. At pressures near 2000 bar and temperatures of 100–300 °C, the reactor contents are dense supercritical or compressed fluids whose density, enthalpy and speed of sound differ markedly from ideal-gas predictions. ISO 4126 [8] is based primarily on ideal-gas critical-flow relations and does not prescribe a complete property treatment for such extreme states. Friedel and Schmidt [9] examined choking in long high-pressure vent lines, while Schmidt et al. [10] showed experimentally and numerically that dense-gas critical mass flux can differ substantially from ideal-gas estimates. Delibalta [11] combined high-pressure autoclave experiments with a single-phase isentropic nozzle model in which flow losses were represented by a discharge coefficient. Dyck and Busch [12] subsequently considered both single- and two-phase high-pressure relief. These studies establish the real-fluid vessel–nozzle model as a useful framework but do not quantify the effect of VA composition over the industrial range.

Two gaps remain. First, the effects of VA on mixture density, phase boundaries, vessel isentropes and nozzle mass flux have not been systematically evaluated over the industrially relevant range of 0–40 mass%. Second, reported “relief times” often conflate discharge kinetics with thermodynamic termination at the phase boundary. Distinguishing these effects is necessary because the present single-phase model does not describe the subsequent two-phase discharge.

This study applies a transient real-fluid vessel–nozzle model to ethylene/VA mixtures. A rigid, adiabatic and well-mixed vessel is coupled to a quasi-steady isentropic nozzle model, with properties evaluated using the Peng–Robinson equation of state implemented in REFPROP [13–15]. Critical flow is identified by maximizing the admissible single-phase mass flux rather than imposing an ideal-gas critical-pressure ratio [16]. The objectives are to: (i) quantify the effects of VA fraction, initial pressure, initial temperature and discharge coefficient; (ii) distinguish discharge kinetics from termination at the phase boundary; and (iii) clarify when the calculated flux maximum represents genuine sonic choking and when it is constrained by the single-phase boundary.

2. Model Formulation

2.1. Physical System and Assumptions

Figure 1 shows the single-phase pressure-relief system considered in this study. The model couples transient depressurization of a rigid, well-mixed vessel with quasi-steady one-dimensional flow through a relief-nozzle throat.

The model is based on the following assumptions:

- (a) The vessel volume V is constant (rigid vessel, no moving boundary).
- (b) The relief event is short, so heat transfer between the vessel contents, the wall and the surroundings is neglected (adiabatic vessel). For the 200 mL autoclave case considered in this study (wetted wall area $2.3 \times 10^{-2} \text{ m}^2$, fluid-side coefficient $h = 50\text{--}500 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$), the wall heat-transfer time is 50–500 s, approximately 14–140 times longer than the longest modeled transient (3.56 s at $T_0 = 300 \text{ °C}$). The estimated wall-to-fluid heat transfer over the longest transient is 0.7–7 kJ, corresponding to approximately 1–11% of the calculated internal-energy decrease. For the natural-convection range $h = 50\text{--}100 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, the contribution is below 3%. The adiabatic assumption is therefore most appropriate for the shorter transients and for natural-convection

conditions; the high-temperature, long-duration cases remain more sensitive to wall heat transfer.

- (c) Pressure perturbations traverse the vessel on the acoustic time scale $L/a = 0.1\text{--}0.6$ ms, which is comparable to or shorter than the 1 ms numerical time step and much shorter than the overall discharge duration. This estimate supports the use of a spatially uniform pressure field. The well-mixed temperature and composition assumptions remain modeling approximations because local thermal, compositional and buoyancy-driven gradients are not resolved.
- (d) The discharged stream has the same composition as the vessel contents, so composition fractionation and spatial segregation are not considered.
- (e) The vessel contents follow an isentropic path during single-phase discharge, as demonstrated in Section 2.2.
- (f) The model is restricted to homogeneous single-phase states: the phase condition is checked during every vessel- and throat-property evaluation, and the calculation is terminated when the vessel state enters the two-phase region, i.e., when the vapor quality Q satisfies $0 < Q < 1$.

Because two-phase throat states are not evaluated by the present nozzle model, the endpoint of a trajectory represents the limit of the single-phase formulation and should not be interpreted as complete depressurization to the back pressure.

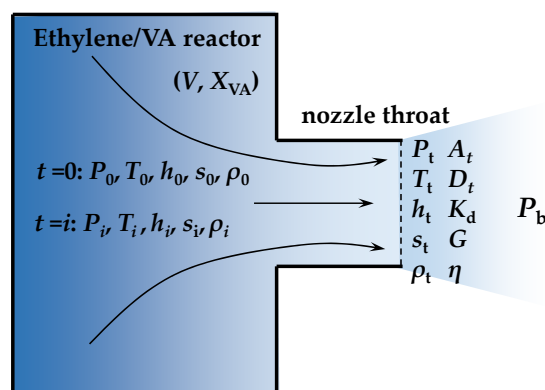


Figure 1. Schematic of pressure relief from a vessel containing an ethylene/VA mixture.

2.2. Vessel Conservation Equations and Isentropic Trajectory

For an adiabatic, rigid vessel with one outlet, the transient mass and energy balances may be written as

$$\frac{dm}{dt} = -q_{out} \quad (1)$$

$$\frac{d(mu)}{dt} = -q_{out} h, \quad (2)$$

where m , u , and h are the mass, specific internal energy, and specific enthalpy of the fluid remaining in the vessel, and q_{out} is the discharge mass flow rate. Combining Equations (1) and (2) gives

$$mdu = (h - u)dm = pvd m. \quad (3)$$

For a constant vessel volume, $v = V/m$, and $dv = -(v/m) \cdot dm$. Substitution of Equations (1) and (2) into the Gibbs relation, $T \cdot ds = du + P \cdot dv$, gives $ds = 0$. Hence, the fluid remaining in the vessel follows the initial isentrope, $s = s_0$, while the assumptions of adiabatic, homogeneous and single-phase discharge remain valid.

2.3. Nozzle-Flow Formulation and Maximum-Flux Condition

At each time step, the vessel state is taken as the stagnation state immediately upstream of the relief nozzle. Expansion from the vessel to a trial throat pressure is assumed to be isentropic, such that

$$s_t = s_i, \quad (4)$$

where the subscripts i and t denote the instantaneous vessel and throat states, respectively. Neglecting upstream kinetic energy, the throat velocity follows from the steady-flow energy equation:

$$u_t = \sqrt{2(h_i - h_t)}. \quad (5)$$

The corresponding ideal isentropic mass flux is given by

$$G(P_t) = \rho_t \sqrt{2(h_i - h_t)}, \quad (6)$$

where h_i is the specific enthalpy of the reactor contents and ρ_t and h_t are evaluated at (P_t, s_i) . For a specified vessel state, the trial throat pressure is varied over

$$P_b \leq P_t < P_i, \quad (7)$$

where P_b is the downstream back pressure. The maximum admissible mass flux is

$$G_{\max,i} = \max_{P_b \leq P_t < P_i} G(P_t). \quad (8)$$

If the maximum is attained at an interior pressure, and the corresponding throat state satisfies $u_t/a_t \approx 1$, the flow is classified as genuinely sonic. The pressure associated with the largest admissible mass flux is denoted by $P_{t,\max,i}$. It is denoted by $P_{t,\text{crit},i}$ only when the maximum is internal and $u_t/a_t \approx 1$. The instantaneous maximum-flux pressure ratio is then

$$\eta_i = \frac{P_{t,\max,i}}{P_i}. \quad (9)$$

If the maximum occurs at the phase-boundary edge, it is classified as phase-boundary-limited and should not be interpreted as conventional sonic choking. If it occurs at $P_t = P_b$, the flow is classified as back-pressure-limited.

2.4. Mass Discharge and Vessel-State Update

The mass discharged over a time step Δt is calculated as

$$\Delta m_i = K_d A_t G_{\max,i} \Delta t, \quad (10)$$

$$A_t = \frac{\pi D_t^2}{4}, \quad (11)$$

where K_d is the discharge coefficient, and A_t and D_t are the throat area and diameter. The throat state is evaluated as an ideal isentropic state, and K_d scales only the mass-removal rate; i.e., the nozzle is treated as an isentropic nozzle of effective area $K_d A_t$. The effects of friction, contraction and other real-nozzle losses are not resolved explicitly; their combined influence on the mass flow is represented empirically by K_d .

The reactor mass and density are updated according to

$$m_{i+1} = m_i - \Delta m_i, \quad (12)$$

$$\rho_{i+1} = \frac{m_{i+1}}{V}, \quad (13)$$

where V is the reactor volume. The new pressure, temperature, and enthalpy are then obtained from a density–entropy flash at (ρ_{i+1}, s_0) . Equations (1)–(13) therefore couple the real-fluid thermodynamic trajectory in the vessel to the instantaneous nozzle-flow condition.

2.5. Thermodynamic Property Model

Thermodynamic properties were calculated using the Peng–Robinson (PR) equation of state implemented in REFPROP 10. The PR framework was selected because it can be applied consistently to both ethylene and the user-defined VA component over the complete parametric campaign and is computationally compatible with the required flash calculations. Previous high-pressure ethylene studies indicate that it can reproduce relief-relevant pure-ethylene properties with useful engineering accuracy [11,16].

VA was represented by a user-defined REFPROP fluid file with $T_c = 519.13$ K, $P_c = 4.185$ MPa, acentric factor $\omega = 0.3767$, and molar mass $M = 86.089$ g·mol^{−1}. The ideal-gas heat capacity was correlated from NIST Chemistry WebBook data. Mixture properties were calculated using the classical van der Waals one-fluid mixing rules with a single binary interaction parameter, k_{ij} . Because no validated value was found for ethylene/VA at the investigated conditions, $k_{ij} = 0$ was used as the reference value and its influence was evaluated in Section 5.1. Because suitable high-pressure ethylene/VA mixture data are unavailable, the absolute mixture-property and phase-boundary predictions remain model-dependent. The resulting relief predictions should therefore be interpreted primarily as comparative trends within the PR framework.

2.6. Numerical Implementation

The model is implemented in MATLAB R2023b using the following procedure.

1. Initialization. A temperature–pressure flash at (T_0, P_0, X_{VA}) provides the initial density ρ_0 , specific enthalpy h_0 , specific entropy s_0 , and phase state. The initial vessel inventory is calculated as $m_0 = \rho_0 V$. The calculation proceeds only if the initial state is single-phase.
2. Throat-state calculation. At time step i , trial throat pressures are generated between P_b and $0.999P_i$. For each pressure, a pressure–entropy flash at (P_t, s_i) provides T_t , ρ_t , h_t , and the phase state. Equation (6) is evaluated for admissible single-phase states satisfying $h_i \geq h_t$.
3. Flow-regime identification and mass update. The largest admissible value of G is selected. An interior maximum with $u_t/a_t \approx 1$ is classified as sonic choking; a maximum at the phase-boundary edge is classified as phase-boundary-limited; and a maximum at $P_t = P_b$ is classified as back-pressure-limited. The discharged mass is calculated from Equation (10), and the time step is reduced if necessary to prevent $\Delta m_i \geq m_i$ or to resolve the approach to a termination boundary.
4. Vessel-state update. A density–entropy flash at (ρ_{i+1}, s_0) provides T_{i+1} , P_{i+1} , h_{i+1} , and the vessel phase state.
5. Termination. The calculation is terminated when (a) phase separation is detected in the vessel, (b) no physically admissible single-phase throat solution can be obtained, (c) the vessel inventory is exhausted, (d) the specified low-pressure threshold is reached, or (e) the prescribed maximum simulation time is exceeded. The active termination criterion is recorded for each simulation.

The reference back pressure is 1.01325 bar. A temporal resolution of 1 ms and 300 throat-pressure scan points were used for all calculations reported below. The parametric campaign consists of the 17 cases listed in Table A1 in Appendix A, organized as four one-factor sweeps around a common base case ($X_{VA} = 10\%$, $P_0 = 2000$ bar, $T_0 = 100$ °C, $K_d = 0.68$). The vessel volume is $V = 2.0 \times 10^{-4}$ m³ (200 mL), and the nozzle throat diameter is $D_t = 1$ mm in all cases.

Numerical convergence was assessed for the base case and the shortest simulated event using time steps of 1.0, 0.5 and 0.25 ms and 300–1200 throat-pressure points. Relative to the reference setting of 1 ms and 300 points, refinement changed the duration by less than 0.9%, the terminal pressure by less than 0.1% and the maximum mass flux by less than 0.001%. Continuous refinement of representative flux maxima by a golden-section search changed G_{max} by no more than 0.14%. The reference discretization was therefore retained.

3. Model Validation

The model was assessed against the high-pressure autoclave experiment reported by Delibalta [11]. The selected case used a 200 mL vessel, an initial pressure of 2000 bar, an initial temperature of 25 °C and a 1 mm nozzle throat. A discharge coefficient of $K_d = 0.68$, reported by Delibalta for a geometrically comparable nozzle, was used without refitting to the pressure trace examined here. The comparison therefore assesses the transferability of the reported coefficient and the vessel–nozzle formulation rather than fitting K_d to the present curve.

Figure 2 compares the measured and calculated pressure histories and pressure–temperature trajectories. Over the measured single-phase interval of 0–312 ms, the pressure comparison gives a root-mean-squared error (RMSE) of 120 bar, a mean absolute error (MAE) of 97 bar, a maximum absolute deviation of 238 bar at approximately 31 ms, and $R^2 = 0.93$. The model systematically overpredicts the vessel pressure and therefore underpredicts the depressurization rate. Possible sources include the use of a constant discharge coefficient, the homogeneous and isentropic vessel assumptions, uncertainty in the effective flow area and limitations of the PR equation of state.

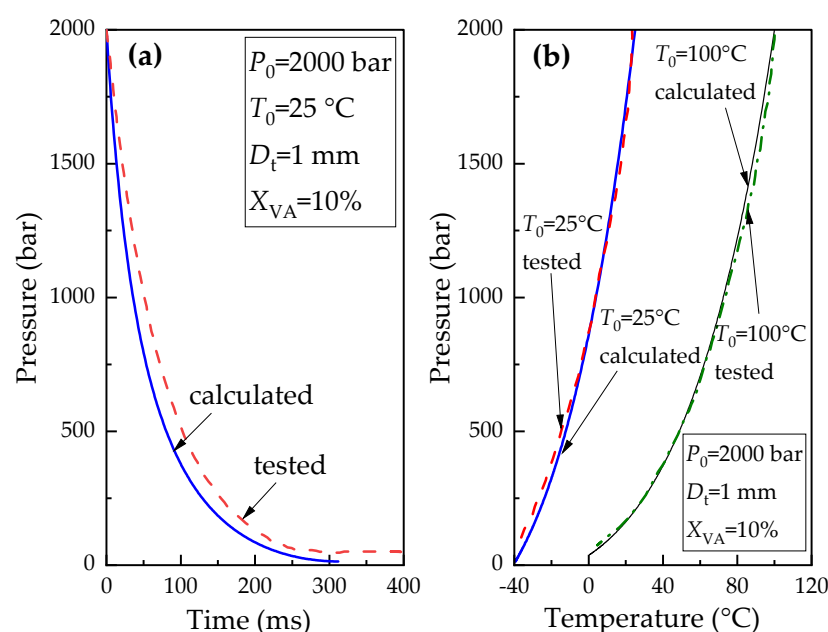


Figure 2. Comparison of measured and calculated (a) vessel pressure–time histories and (b) vessel pressure–temperature trajectories for experiments reported by Delibalta [11].

The experimental curve was digitized from Ref. [11] because tabulated data were unavailable. The estimated digitization uncertainty is below 1% of the pressure-axis range and approximately 1 ms in time; the source provides no complete measurement-uncertainty budget. The comparison supports use of the model for comparative analysis near the validated condition, but it does not validate the full ranges of composition, pressure and temperature examined below.

4. Results

4.1. Effect of VA Mass Fraction

Figures 3 and 4 compare mixtures with VA mass fractions of 0–40% at $P_0 = 2000$ bar, $T_0 = 100$ °C, $D_t = 1$ mm and $K_d = 0.68$.

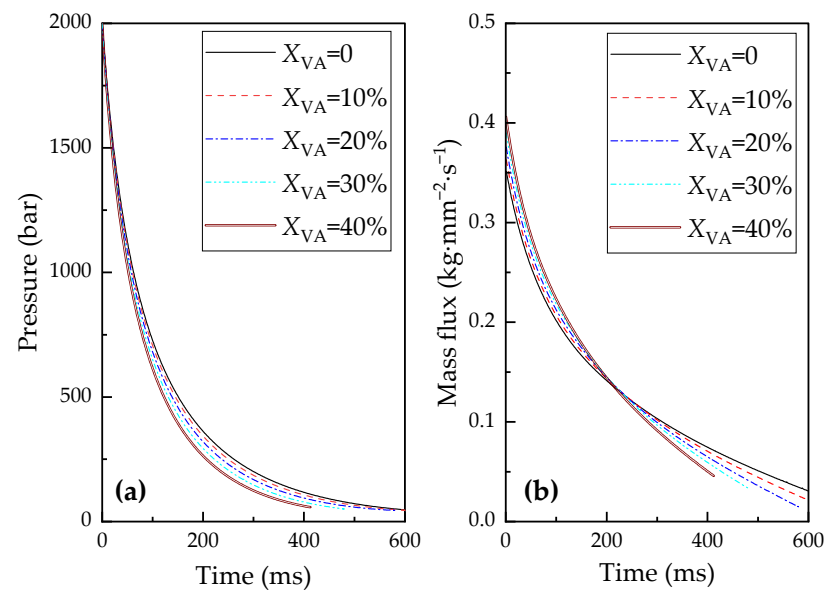


Figure 3. Effects of VA mass fraction on (a) vessel pressure and (b) ideal maximum mass flux as functions of time ($P_0 = 2000$ bar, $T_0 = 100$ °C, $D_t = 1$ mm, $K_d = 0.68$).

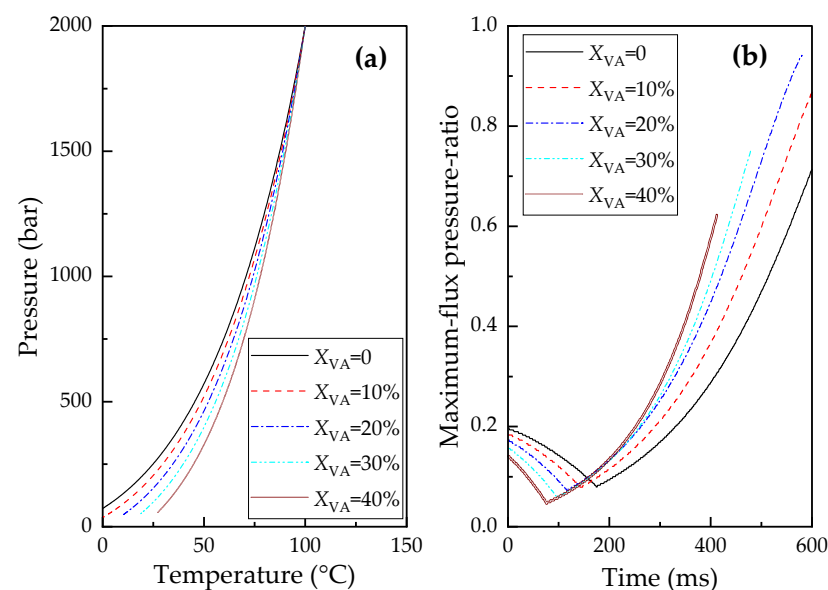


Figure 4. Effects of VA mass fraction on (a) vessel pressure–temperature trajectories and (b) maximum-flux pressure-ratio–time trajectories ($P_0 = 2000$ bar, $T_0 = 100$ °C, $D_t = 1$ mm, $K_d = 0.68$).

Increasing X_{VA} accelerates the pressure decrease and shortens the modeled single-phase duration from 761 ms for pure ethylene to 413 ms at $X_{VA} = 40\%$ [Figure 3a]. At 200 ms, the calculated vessel pressure decreases from 362 bar for pure ethylene to 263 bar for the 40% VA mixture. The ideal maximum mass flux decreases throughout each trajectory as the vessel depressurizes [Figure 3b]. Its initial value increases from 0.35 to 0.41 $\text{kg}\cdot\text{mm}^{-2}\cdot\text{s}^{-1}$ as X_{VA} increases from 0 to 40%. The faster pressure decay at high VA content reflects the combined effects of mass flux, initial inventory and mixture compressibility; it cannot be inferred from mass flux alone.

Increasing the VA fraction also shifts the vessel isentrope and its intersection with the predicted phase boundary [Figure 4a]. The terminal single-phase pressure increases from 33.6 to 55.8 bar and the corresponding temperature from -8.7 to 27.3 °C. These states mark the end of the single-phase calculation rather than completion of the relief event. Figure 4b shows the pressure ratio associated with the largest admissible single-phase mass flux. The initial ratio ranges from 0.14 to 0.20. Near termination, it increases to 0.62–1.00 because the admissible pressure interval becomes constrained by the phase boundary. As shown in Section 5.2, these terminal maxima are not necessarily sonic and should not all be interpreted as conventional critical-pressure ratios.

4.2. Effect of Initial Pressure

Figures 5 and 6 show results for initial pressures of 500, 1000, 2000, and 3000 bar at $T_0 = 100$ °C, $D_t = 1$ mm, $K_d = 0.68$, and $X_{VA} = 10\%$.

Increasing P_0 from 500 to 3000 bar shortens the modeled duration from 1271 to 603 ms, although the reduction is not proportional to the increase in initial pressure [Figure 5a]. Over this range, the initial inventory increases by 42%, the initial mass flux rises from 0.14 to 0.47 $\text{kg}\cdot\text{mm}^{-2}\cdot\text{s}^{-1}$, and the terminal pressure varies non-monotonically from 32.6 to 50.5 bar. The higher mass flux outweighs the larger inventory and wider pressure interval, but these competing effects limit the reduction in duration. The mass-flux curves decrease and eventually approach one another because the quasi-steady nozzle calculation depends on the instantaneous vessel state rather than directly on P_0 [Figure 5b]. Their cross-over near 400–600 ms does not imply identical pressure histories: according to Equation (19), the pressure-decay rate also depends on the vessel sound speed, while the remaining inventory and isentrope differ among cases.

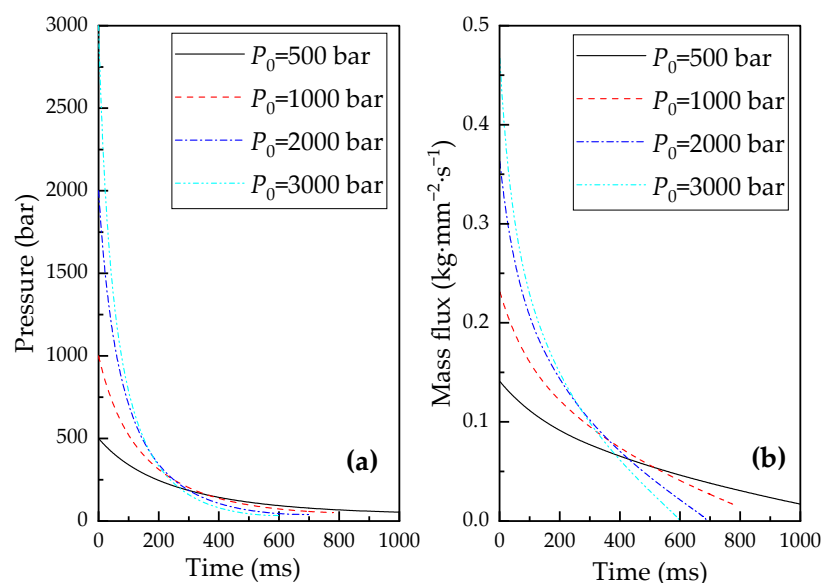


Figure 5. Effects of initial pressure on (a) vessel pressure and (b) ideal maximum mass flux as functions of time ($T_0 = 100$ °C, $D_t = 1$ mm, $K_d = 0.68$, $X_{VA} = 10\%$).

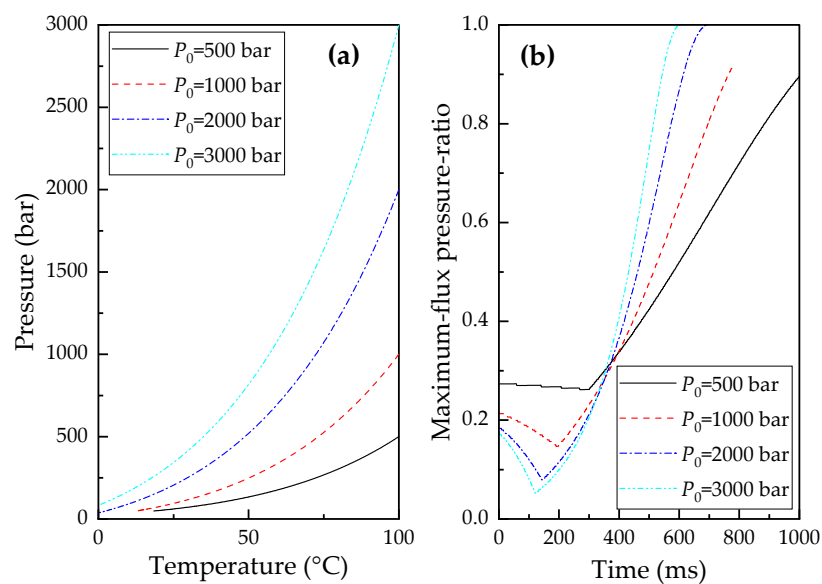


Figure 6. Effects of initial pressure on (a) vessel pressure–temperature trajectories and (b) maximum-flux pressure-ratio–time trajectories ($T_0 = 100$ °C, $D_t = 1$ mm, $K_d = 0.68$, $X_{VA} = 10\%$).

The pressure–temperature trajectories in Figure 6a show a greater overall temperature decrease when a larger pressure interval is traversed. At a common vessel pressure, however, the temperatures need not be identical because each simulation follows an isentrope determined by its own initial state. Across the investigated cases, the terminal pressures range from 32.6 to 50.5 bar, and the terminal temperatures range from -7.7 to 18.4 °C. Figure 6b again demonstrates that the maximum-flux pressure ratio is state-dependent. The 3000-bar case lies outside the validated condition and should therefore be interpreted as a comparative model prediction rather than a quantitatively validated result.

4.3. Effect of Initial Temperature

Figures 7 and 8 compare initial temperatures of 25, 100, 200, and 300 °C at $P_0 = 2000$ bar, $D_t = 1$ mm, $K_d = 0.68$, and $X_{VA} = 10\%$.

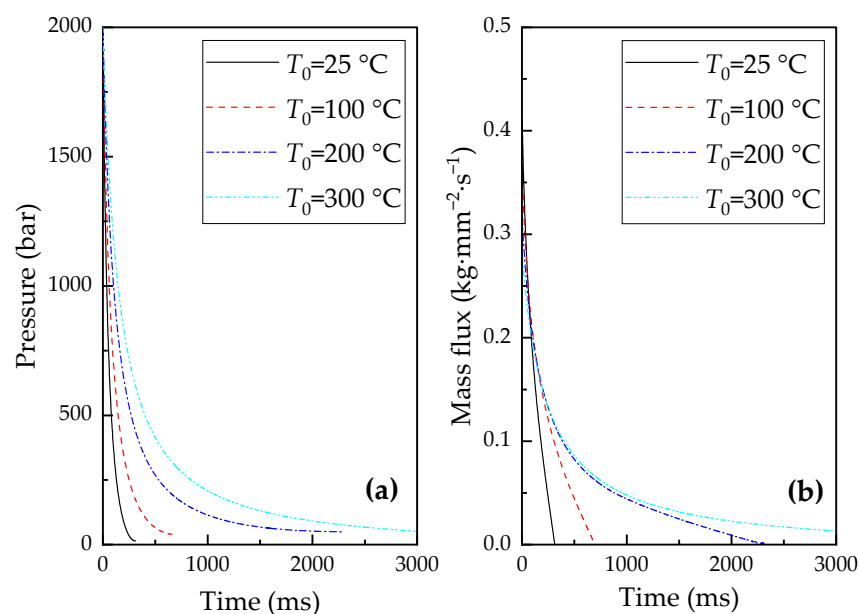


Figure 7. Effects of initial temperature on (a) vessel pressure and (b) ideal maximum mass flux as functions of time ($P_0 = 2000$ bar, $D_t = 1$ mm, $K_d = 0.68$, $X_{VA} = 10\%$).

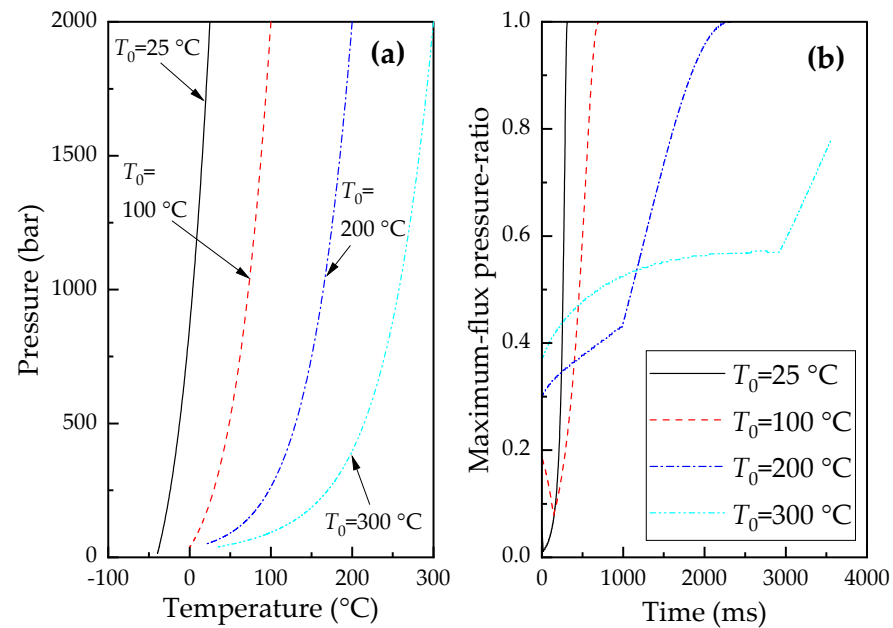


Figure 8. Effects of initial temperature on (a) vessel pressure–temperature trajectories and (b) maximum-flux pressure-ratio–time trajectories ($P_0 = 2000$ bar, $D_t = 1$ mm, $K_d = 0.68$, $X_{VA} = 10\%$).

Increasing T_0 from 25 to 300 °C extends the modeled duration from 312 to 3555 ms [Figure 7a], although the initial inventory decreases from 121.9 to 99.5 g. The longer duration therefore cannot be attributed to inventory alone; it results from the lower mass flux, the different isentropic compressibility and the location of the phase-boundary intersection. Common-pressure arrival times are compared in Section 5.5 to separate these effects from differences in the endpoint. The initial maximum mass flux decreases monotonically from 0.41 to 0.28 kg·mm⁻²·s⁻¹ as T_0 increases from 25 to 300 °C [Figure 7b]. The mass discharged before phase-boundary termination also changes substantially because both the initial density and the terminal state depend on temperature.

Figure 8a shows cooling along all four isentropic trajectories. Their predicted terminal pressures are 14.2, 39.0, 50.0, and 39.2 bar at initial temperatures of 25, 100, 200, and 300 °C, respectively. The non-monotonic terminal pressure demonstrates that the extent of the modeled single-phase interval cannot be inferred from initial temperature alone; it is determined by the intersection of each initial-state isentrope with the mixture phase boundary. The 200 and 300 °C cases have the longest durations and are therefore the most sensitive to the adiabatic assumption. The heat-transfer estimate in Section 2.1 indicates a small correction under natural-convection conditions, but the quantitative high-temperature results remain more uncertain than the shorter-duration cases.

4.4. Effect of Discharge Coefficient

Figures 9 and 10 isolate the effect of the discharge coefficient K_d (0.5, 0.68, 0.8, 1.0) at $P_0 = 2000$ bar, $T_0 = 100$ °C, $D_t = 1$ mm, and $X_{VA} = 10\%$.

The discharge coefficient appears only in the mass-removal equation and therefore changes the rate at which the vessel traverses a fixed isentrope. Increasing K_d from 0.50 to 1.00 reduces the modeled duration from 949 to 473 ms [Figure 9a] but leaves the terminal state unchanged. Figure 9b reports the ideal maximum mass flux before multiplication by K_d . Consequently, all cases have the same $G_{\max}$ at a given vessel state; differences in the time-domain curves arise solely from the different rates at which those states are reached. The actual mass-flow rate, $K_d \cdot A_t \cdot G_{\max}$, scales linearly with K_d . Consistent with this formulation, the pressure–temperature trajectories coincide and the pressure-ratio trajectories

collapse when plotted against a vessel-state variable rather than physical time (Figure 10). Thus, K_d controls the time scale but not the modeled isentrope, endpoint or state-specific ideal mass flux.

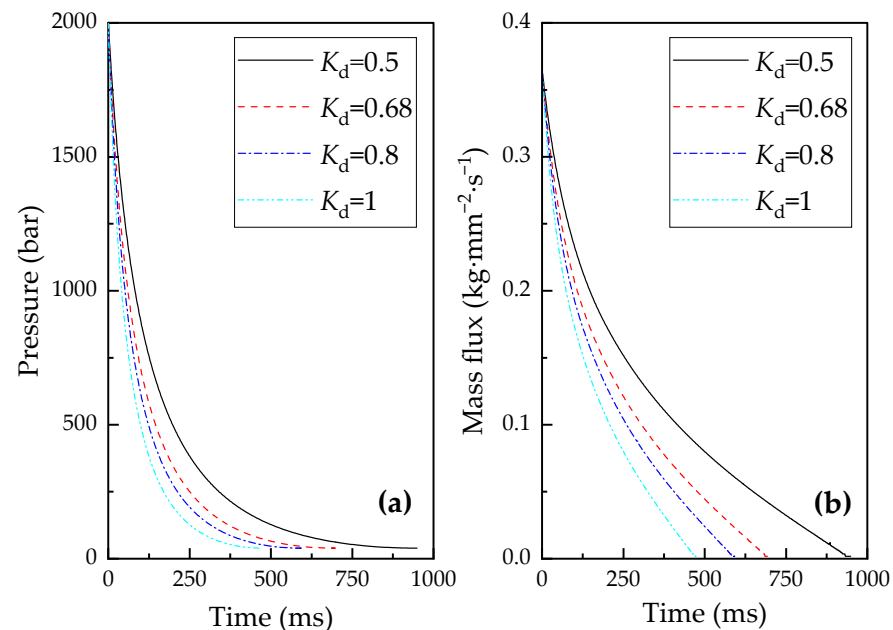


Figure 9. Effects of discharge coefficient on (a) vessel pressure and (b) ideal maximum mass flux as functions of time ($P_0 = 2000$ bar, $T_0 = 100$ °C, $D_t = 1$ mm, $X_{VA} = 10\%$).

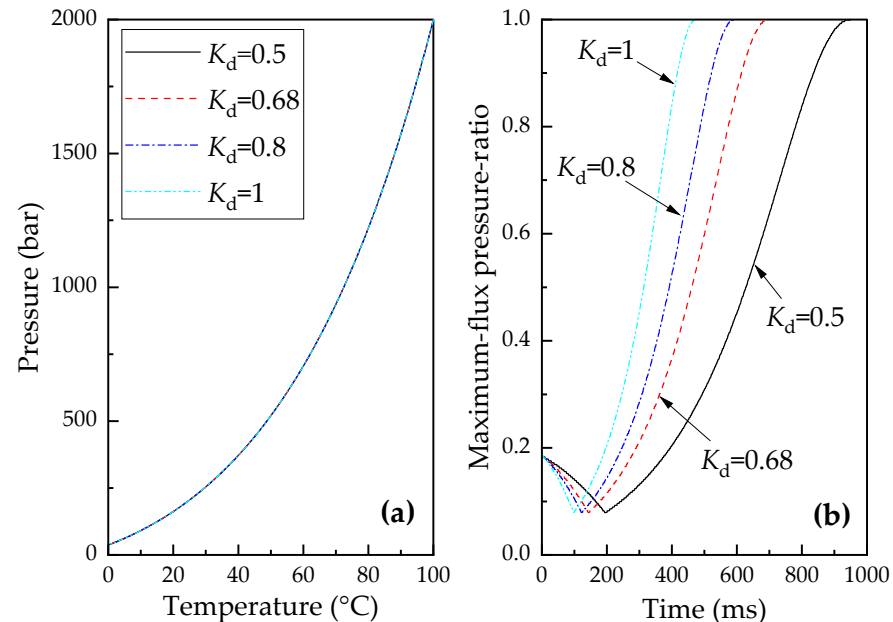


Figure 10. Effects of discharge coefficient on (a) vessel pressure–temperature trajectories and (b) maximum-flux pressure-ratio–time trajectories ($P_0 = 2000$ bar, $T_0 = 100$ °C, $D_t = 1$ mm, $X_{VA} = 10\%$).

5. Discussion

Table A1 summarizes the initial conditions and calculated outputs for all cases. The following sections examine property-model sensitivity, pressure-decay mechanisms, choking and termination regimes, time-scale behavior and the limitations of the single-phase formulation.

5.1. Sensitivity to the Binary Interaction Parameter

The sensitivity to k_{ij} was evaluated at $X_{VA} = 10\%$ and 40% for $k_{ij} = 0, 0.02, 0.05$ and 0.10 , as shown in Table 1. At $k_{ij} = 0.05$, the initial density and mass flux change by less than 0.2% and 0.6% , respectively, while the terminal pressure changes by no more than 2.2% . The duration increases by 2.2% at 10% VA and 7.5% at 40% VA. Even at $k_{ij} = 0.10$, the initial density, initial mass flux and terminal pressure change by no more than 0.4% , 1.3% and 4.3% , respectively, whereas the duration increases by 4.6% and 15.0% .

The calculated ordering—higher initial mass flux and shorter duration at higher VA content—is preserved over the tested range of k_{ij} . The qualitative composition trend is therefore robust within the PR mixing framework, but the absolute duration at high VA content remains sensitive to the assumed interaction parameter. In the absence of high-pressure ethylene/VA mixture data, this sensitivity analysis bounds model dependence but does not constitute experimental validation.

Table 1. Sensitivity of selected outputs to the ethylene–VA binary interaction parameter at $P_0 = 2000$ bar and $T_0 = 100$ °C.

X_{VA}	k_{ij}	ρ_0 (kg·m ^{−3})	m_0 (g)	G_0 (kg·mm ^{−2} ·s ^{−1})	t_{end} (ms)	P_{end} (bar)	T_{end} (°C)	ω (%)
10%	0.00	577.70	115.54	0.3630	697	39.02	0.43	34.58
10%	0.02	577.56	115.51	0.3627	703	38.67	0.03	34.77
10%	0.05	577.36	115.47	0.3623	712	38.16	−0.59	35.04
10%	0.10	577.02	115.40	0.3616	729	37.34	−1.62	35.50
40%	0.00	670.40	134.08	0.4059	413	55.80	27.27	26.64
40%	0.02	669.95	133.99	0.4049	425	55.76	26.54	27.01
40%	0.05	669.28	133.86	0.4034	444	55.98	25.45	27.58
40%	0.10	668.16	133.63	0.4010	475	57.03	23.70	28.50

5.2. Decoupling the Drivers of Pressure Decay

The transient pressure response is governed by the coupling between the thermodynamic response of the vessel contents and the hydraulic discharge capacity of the relief nozzle. In the present model, the vessel remains rigid and follows an isentropic path during the single-phase discharge. Therefore, for a specified composition,

$$m = \rho V. \quad (14)$$

The mass balance is

$$\frac{dm}{dt} = -K_d \cdot A_t \cdot G. \quad (15)$$

Differentiating the vessel inventory relation along the isentrope gives

$$\frac{dm}{dt} = V \left(\frac{\partial \rho}{\partial P} \right)_s \frac{dP}{dt}. \quad (16)$$

Combining the mass balance and the thermodynamic relation yields the pressure-decay equation

$$\frac{dP}{dt} = - \frac{K_d A_t G}{V} \frac{1}{\left(\frac{\partial \rho}{\partial P} \right)_{s, X_{VA}}}. \quad (17)$$

For a stable single-phase fluid, the isentropic speed of sound is defined by

$$a_s^2 = \left(\frac{\partial P}{\partial \rho} \right)_{s, X_{VA}}, \quad (18)$$

where a_s is the isentropic speed of sound evaluated at the instantaneous vessel state. Hence Equation (17) changes into

$$\frac{dP}{dt} = - \frac{K_d A_t G}{V} a_s^2. \quad (19)$$

Equation (19) separates the hydraulic and thermodynamic contributions to vessel depressurization. The mass flux determines the rate of mass removal, whereas $a_s^2 = (\partial P / \partial \rho)_s$, evaluated at the instantaneous vessel state, determines the pressure response to a density change along the vessel isentrope. Similar nozzle mass fluxes can therefore produce different pressure-decay rates when the vessel sound speeds differ. Initial inventory and the terminal phase boundary further determine the elapsed time over a finite pressure interval.

The nature of the calculated flux maximum was examined from $G(P_t)$ and the corresponding throat ratio u_t/a_t (Figure 11). During the high-pressure stage, $G(P_t)$ has a smooth interior maximum above the saturation pressure, and u_t/a_t remains close to unity. For $X_{VA} = 10\%$, $u_t/a_t = 0.98\text{--}1.004$ until approximately 149 ms ($P \approx 490$ bar); comparable behavior is obtained for $X_{VA} = 40\%$. These states represent genuine sonic choking.

At lower vessel pressures, the unconstrained sonic throat state would lie beyond the admissible single-phase domain. The largest admissible flux is then attained at the phase-boundary edge, $P_{t,\max} \approx P_{\text{sat}}$, with $u_t/a_t < 1$. Consequently, the near-unity terminal pressure ratios in Table A1 identify phase-boundary-limited maxima rather than sonic choking.

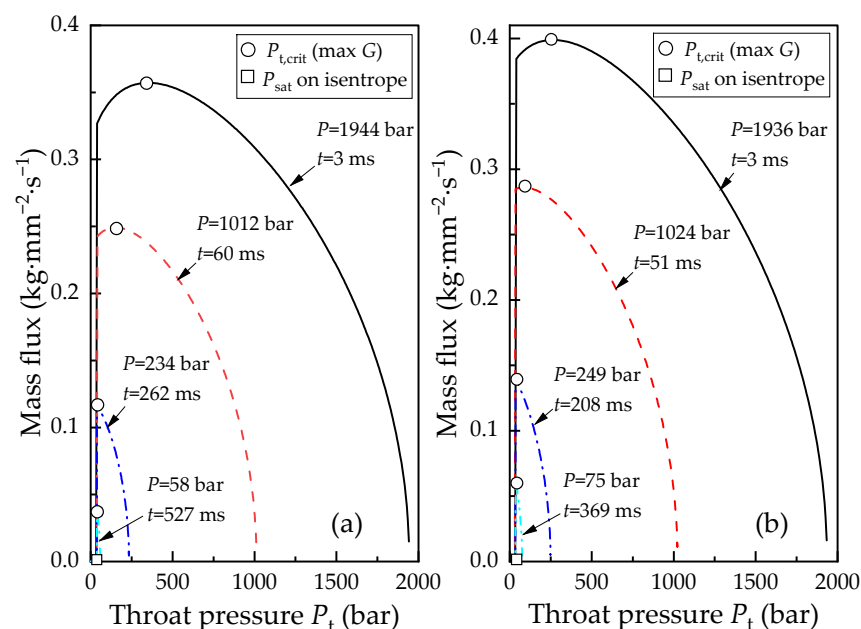


Figure 11. Isentropic mass flux $G(P_t)$ at four representative vessel states for (a) $X_{VA} = 10\%$ and (b) $X_{VA} = 40\%$. Open circles denote the identified admissible maxima and filled squares denote the saturation pressures along the corresponding vessel isentropes. Early-stage maxima are sonic ($u_t/a_t \approx 1$); near-termination maxima are constrained by the phase boundary.

5.3. Choking and Termination Regimes of the Modeled Single-Phase Segment

At the reference back pressure of 1.01325 bar, the pressure associated with the largest admissible mass flux remains between 14.2 and 49.9 bar at its minimum across the

investigated cases. The back pressure therefore does not constrain the modeled trajectories. At high vessel pressure the flow is sonically choked; near termination the admissible maximum may instead be limited by the phase boundary. In either regime, the single-phase calculation ends at the vessel phase boundary rather than through equalization with the reference back pressure.

Raising the back pressure can alter this behavior. At $P_b = 10$ bar, the base-case trajectory and endpoint remain essentially unchanged because the admissible maximum-pressure state stays above the back pressure. At $P_b = 50$ bar, the base case and the 300 °C case become back-pressure-limited before reaching their single-phase phase-boundary pressures of approximately 39 bar. The 40% VA case, whose phase boundary lies at 55.8 bar, still terminates at the phase boundary, although its late-stage flow rate is reduced. Thus, the reference conclusions are robust at low back pressure but cannot be generalized to systems whose back pressure approaches the minimum admissible throat pressure.

5.4. Quantitative Verification of Discharge-Time Scaling with K_d

For simulations that follow the same vessel-state trajectory and terminate at the same state, the elapsed time is inversely proportional to the discharge coefficient:

$$K_{d,2}t(K_{d,2}) \approx K_{d,1}t(K_{d,1}). \quad (20)$$

Finite time stepping and event detection introduce only small numerical deviations from this scaling. When pressure is plotted against the rescaled time $K_d \cdot t$, the four discharge-coefficient cases collapse onto a single curve (Figure 12). This confirms that K_d changes the time scale but not the state-space trajectory or endpoint. A state-dependent discharge coefficient could be incorporated in future work, although it would remove the simple constant- K_d scaling.

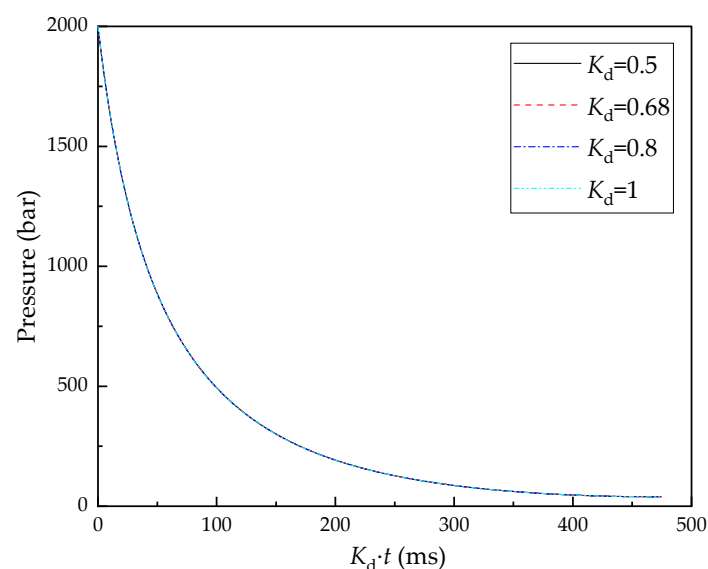


Figure 12. Vessel pressure as a function of the rescaled time $K_d \cdot t$ for different discharge coefficients ($P_0 = 2000$ bar, $T_0 = 100$ °C, $D_t = 1$ mm, $X_{VA} = 10\%$).

5.5. Separating Discharge Kinetics from Thermodynamic Termination

The terminal duration combines two effects: the rate of mass removal and the position at which the vessel isentrope meets the phase boundary. Common-pressure arrival times provide a kinetic comparison independent of the final pressure (Figure 13). For example, the time to reach 100 bar ranges from 280 ms at $K_d = 1.00$ to 561 ms at $K_d = 0.50$, and

from 190 ms at $T_0 = 25^\circ\text{C}$ to 1871 ms at 300°C . The fraction of the initial inventory discharged before phase-boundary termination ranges from 19.8% to 87.0%.

The 25°C case reaches a common pressure fastest even though it has the lowest terminal pressure. Its liquid-like isentrope produces a large pressure decrease from a relatively small density and inventory change. This result illustrates why terminal duration, common-pressure arrival time and discharged mass fraction should be reported separately.

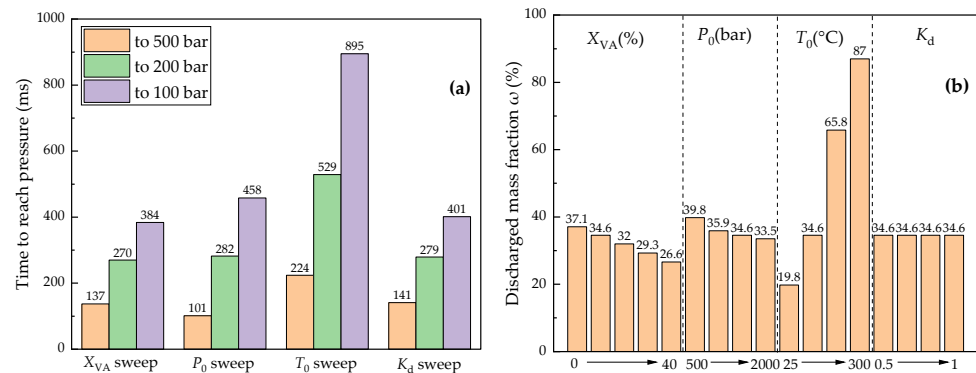


Figure 13. Time required to reach a set of common pressures (a) and the fraction of initial inventory discharged within the single-phase segment (b).

5.6. Implications of the Neglected Two-Phase Stage

The calculation ends when the vessel reaches the predicted phase boundary and therefore does not describe complete depressurization. The terminal vessel pressure is 14.2–55.8 bar, substantially above the reference back pressure, and 13.0–80.2% of the initial inventory remains in the vessel, depending on the case. The omitted two-phase stage is therefore minor for some high-temperature cases but dominant in terms of residual inventory for the 25°C and other liquid-like cases.

The reported duration is consequently a lower bound on the total depressurization time. No general quantitative bound on the duration of the omitted stage can be established from the terminal mass flux alone because two-phase critical flow, flashing, heat transfer and the continuously decreasing driving pressure are not represented. Likewise, the present single-phase mass flux should not be described as a rigorous upper bound without a validated two-phase model. The parametric conclusions apply only to the modeled single-phase segment; complete relief sizing requires a coupled two-phase vessel–nozzle calculation.

6. Conclusions

A transient real-fluid vessel–nozzle model was developed to describe the single-phase pressure relief of ethylene/VA mixtures under high-pressure polyethylene process conditions. The main conclusions are as follows:

- (1) For the published validation case at 2000 bar and 25°C , the model reproduced the measured pressure-decay trend with $RMSE = 120$ bar, $MAE = 97$ bar and $R^2 = 0.93$. The systematic pressure overprediction and the single validation condition limit the model to comparative analysis rather than unrestricted quantitative prediction.
- (2) Increasing the VA mass fraction from 0 to 40% raised the initial maximum mass flux from 0.35 to 0.41 $\text{kg}\cdot\text{mm}^{-2}\cdot\text{s}^{-1}$ and shortened the modeled duration from 761 to 413 ms. It also increased the predicted terminal pressure from 33.6 to 55.8 bar by shifting the phase-boundary intersection.

- (3) Increasing the initial pressure from 500 to 3000 bar raised the initial mass flux from 0.14 to 0.47 kg·mm⁻²·s⁻¹ and reduced the duration from 1271 to 603 ms. Increasing the initial temperature from 25 to 300 °C reduced the initial mass flux from 0.41 to 0.28 kg·mm⁻²·s⁻¹ and extended the duration from 312 to 3555 ms. These durations reflect both discharge kinetics and the location of phase-boundary termination.
- (4) Increasing K_d from 0.50 to 1.00 shortened the modeled duration from 949 to 473 ms but did not change the vessel isentrope, terminal state or state-specific ideal mass flux. For constant K_d , the discharge time scales approximately with $1/K_d$.
- (5) Genuine sonic choking occurred during the high-pressure stage, where the mass-flux maximum was internal, and $u_t/a_t \approx 1$. Near termination, the unconstrained sonic state moved beyond the admissible single-phase domain, and the calculated maximum became phase-boundary-limited. The near-unity terminal pressure ratios therefore do not represent conventional sonic critical-pressure ratios.
- (6) No suitable experimental density or vapor–liquid equilibrium data for ethylene/VA mixtures at pressures up to 3000 bar were identified in the open literature. The k_{ij} sensitivity analysis preserves the qualitative VA trend but changes the duration by as much as 15% at 40% VA.
- (7) The pressure ratio associated with the admissible mass-flux maximum is strongly state- and composition-dependent. Initial values range from 0.05 to 0.37, whereas near-termination values may approach unity because of phase-boundary truncation. Fixed ideal-gas critical-pressure ratios are therefore unsuitable for these mixtures, but the calculated ratio must be interpreted together with the Mach number and phase constraint.

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Abbreviations

The following abbreviations are used in this manuscript:

CFD	Computational Fluid Dynamics
EOS	Equation of state
ISO	International Organization for Standardization
NIST	National Institute of Standards and Technology
PR	Peng–Robinson
REFPROP	Reference Fluid Thermodynamic and Transport Properties Database
VA	Vinyl acetate

Appendix A

Table A1. Initial conditions and calculated single-phase relief characteristics for all simulated cases.

Case No.	X_{VA}	P_0	T_0	K_d	m_0	m_{end}	ω^*	t_{end}	P_{end}	T_{end}	G_0	G_{end}	η_0	η_{end}	a_{s0}	a_{send}	$P_{t,max}^{**}$	$t_{1000}^{\dagger}$	$t_{500}^{\dagger}$	$t_{200}^{\dagger}$	$t_{100}^{\dagger}$
	%	bar	°C	-	g		%	ms	bar	°C	kg·mm ⁻² ·s ⁻¹	-	-	-	m/s	bar		ms			
1	0	2000	100	0.68	110.4	69.5	37.1	761	33.6	−8.7	0.35	0.0015	0.20	1.00	1651	441	33.6	62	151	301	432
2 ⁺⁺	10	2000	100	0.68	115.5	75.6	34.6	697	39.0	0.4	0.36	0.0017	0.18	1.00	1647	462	39.0	60	145	287	412
3	20	2000	100	0.68	121.2	82.4	32.0	580	44.9	9.6	0.38	0.0149	0.17	0.94	1646	484	42.2	58	138	272	389
4	30	2000	100	0.68	127.3	90.0	29.3	480	50.8	18.6	0.39	0.0336	0.16	0.75	1647	513	38.2	55	131	254	360
5	40	2000	100	0.68	134.1	98.4	26.6	413	55.8	27.3	0.41	0.0454	0.14	0.62	1652	543	34.6	52	122	235	328
6	10	500	100	0.68	85.7	51.6	39.8	1271	48.3	18.4	0.14	0.0016	0.27	1.00	743	299	48.2	—	0	271	563
7	10	1000	100	0.68	102.2	65.5	35.9	780	50.5	13.3	0.23	0.0165	0.22	0.92	1097	386	46.3	0	107	302	491
8 ⁺⁺	10	2000	100	0.68	115.5	75.6	34.6	697	39.0	0.4	0.36	0.0017	0.18	1.00	1647	462	39.0	60	145	287	412
9	10	3000	100	0.68	121.9	81.0	33.5	603	32.6	−7.7	0.47	0.0016	0.17	1.00	2108	511	32.6	76	150	268	367
10	10	2000	25	0.68	121.9	97.8	19.8	312	14.2	−39.4	0.41	0.0012	0.05	1.00	1904	723	14.2	36	81	145	190
11 ⁺⁺	10	2000	100	0.68	115.5	75.6	34.6	697	39.0	0.4	0.36	0.0017	0.18	1.00	1647	462	39.0	60	145	287	412
12	10	2000	200	0.68	107.2	36.6	65.8	2309	50.0	20.4	0.32	0.0014	0.30	1.00	1427	246	49.9	101	269	644	1108
13	10	2000	300	0.68	99.5	13.0	87.0	3555	39.2	35.5	0.28	0.0090	0.37	0.78	1295	268	30.5	145	402	1038	1871
14	10	2000	100	0.50	115.5	75.6	34.6	949	39.0	0.4	0.36	0.0017	0.18	1.00	1647	462	39.0	82	198	391	561
15 ⁺⁺	10	2000	100	0.68	115.5	75.6	34.6	697	39.0	0.4	0.36	0.0017	0.18	1.00	1647	462	39.0	60	145	287	412
16	10	2000	100	0.80	115.5	75.6	34.6	592	39.0	0.4	0.36	0.0017	0.18	1.00	1647	462	39.0	51	123	244	350
17	10	2000	100	1.00	115.5	75.6	34.6	473	39.0	0.4	0.36	0.0017	0.18	1.00	1647	462	39.0	41	99	195	280

* $\omega = (m_0 - m_{end})/m_0 \times 100\%$. ** $P_{t,max}$ denotes the throat pressure associated with the largest admissible single-phase mass flux. It represents a sonic critical pressure when $u/a_t \approx 1$. [†]: t_{1000} , t_{500} , t_{200} and t_{100} are the elapsed times at which the vessel pressure first falls to 1000, 500, 200 and 100 bar. ⁺⁺: Cases 2, 8, 11 and 15 represent the same base condition and are repeated only to identify the reference case for each one-factor sweep.

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