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Cryogenic Simulation and Freezing Point Evaluation in Nitrogen Rejection from Natural Gas: A Coupled Aspen HYSYS–ThermoFAST Approach

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Highlights

- Modeling of the smart water flooding process with polymer.
- Laboratory investigation and simulation to improve understanding of the effective mechanisms governing polymer-assisted smart water injection.
- Chemical enhanced oil recovery.
- Polymer–smart water flooding demonstrated a high potential for wettability alteration.
- Polymer–smart water flooding exhibited significant potential to enhance sweep efficiency.

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Abstract

Cryogenic nitrogen rejection from methane-rich natural gas is a critical operation for meeting LNG and pipeline gas specifications. However, it is highly susceptible to operational disturbances caused by solid formation in heat exchangers and distillation columns. This study proposes an integrated simulation framework that couples steady-state process modeling in Aspen HYSYS with rigorous solid–liquid–vapor equilibrium analysis in ThermoFAST to systematically evaluate freezing risks in CH₄–N₂ mixtures under nitrogen-rejection unit conditions. The nitrogen-rejection unit process, including multi-stream heat exchange, Joule–Thomson expansion, and cryogenic distillation, is modeled using the Peng–Robinson equation of state. ThermoFAST employs a Helmholtz-energy-based PC-SAFT equation of state, together with Lennard-Jones Weeks–Chandler–Andersen pure-solid references, to generate freezing envelopes over a wide pressure range of 0.1–10 MPa and across methane-rich to nitrogen-rich compositions relevant to industrial operations.

The framework is validated against available experimental solid–liquid equilibrium data, yielding mean absolute and relative deviations of 3.45 K and 5%, respectively, thereby demonstrating its suitability for hazard screening applications. Simulation results indicate that increasing pressure elevates the eutectic temperature and expands the stability region of the solid phase. In contrast, increasing nitrogen concentration depresses the eutectic temperature and narrows the solid stability range. Risk maps show that solid formation is most probable in methane-rich streams with CH₄ greater than 0.75 at pressures of 10 MPa or higher, as well as in nitrogen-rich streams with CH₄ less than 0.55 at extremely low temperatures, particularly after expansion and on the upper trays of the distillation column. The proposed integrated approach provides a predictive tool for identifying vulnerable operating zones, defining safe temperature–pressure margins, and enhancing the safety, operability, and efficiency of cryogenic nitrogen rejection processes.

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1. Introduction

In recent years, simulation-based approaches have gained significant attention for optimizing gas processing systems, with increasing emphasis on integrating process simulation with rigorous thermodynamic modeling of solid–liquid–vapor equilibria (Hill and Justice, 2011; Luo et al., 2019; Iftakher et al., 2022; Palomar et al., 2024). This integration is particularly critical in cryogenic separation processes, which constitute a cornerstone of modern natural gas treatment, especially in nitrogen rejection units designed to meet the stringent specifications of pipeline gas and liquefied natural gas. One of the most pressing operational challenges in these units is the risk of solid formation, most notably methane–nitrogen solid solutions, at temperatures approaching the freezing limits of the mixture (Sampson et al., 2021; Hidalgo and Martín-Marroquín, 2025). Unexpected solidification can lead to blockages in heat exchangers, valve malfunctions, and costly plant shutdowns. Therefore, accurate prediction of solid–liquid–vapor equilibrium is of paramount importance from both safety and economic perspectives (Stringari et al., 2014; Yang et al., 2022).

The thermodynamic behavior of methane–nitrogen systems at cryogenic temperatures has been extensively investigated experimentally over the past several decades (Yang et al., 2024; Raj and Raj, 2025). Classical studies, such as that of Omar et al. (1962), characterized the eutectic-type solid–liquid equilibrium behavior of N_2 – CH_4 mixtures, revealing partial miscibility in the solid phase and identifying the eutectic point at approximately 62.6 K (Omar et al., 1962). Subsequent investigations extended these measurements to broader composition and pressure ranges, enabling the construction of three-dimensional pressure–temperature–composition phase diagrams (Kouvaris and Flasar, 1991). Additional studies examined freezing point depression in methane-rich liquids containing dissolved nitrogen, demonstrating that the freezing temperature can shift substantially as a function of nitrogen concentration, pressure, and the presence of other hydrocarbons (Richardson et al., 2019).

In parallel with these experimental efforts, thermodynamic modeling of solid–liquid–vapor equilibrium has advanced considerably. Cubic equations of state, such as Peng–Robinson and Soave–Redlich–Kwong, remain attractive for process simulation because of their computational efficiency, particularly when combined with optimized binary interaction parameters derived from high-quality solid–fluid equilibrium data (Soave et al., 2010; Yang et al., 2022). More advanced formulations, notably the Solid–Liquid–Vapor equation of state proposed by Yokozeki, enable a unified representation of solid, liquid, and vapor phases and have been successfully applied to cryogenic mixtures (Campestrini et al., 2014; Stringari et al., 2014). When coupled with molecular-based correlations, these models can capture eutectic, solid-solution, and azeotropic behavior in methane–nitrogen systems. Nevertheless, their integration into flowsheet-based process simulators remains limited, and freezing envelope predictions are rarely incorporated into operational decision-making.

Recent developments have highlighted the importance of combining experimental solid–liquid–vapor equilibrium data with predictive thermodynamic models to mitigate solidification hazards in cryogenic processing. For example, Riva (2016) integrated original experimental measurements with model

calibration for multicomponent mixtures, including $\text{N}_2\text{--CH}_4\text{--CO}_2\text{--O}_2$, providing datasets and validated models that directly support the design of cryogenic upgrading and liquefaction processes (Riva, 2016).

Nevertheless, a persistent gap remains. Although the binary phase behavior of methane–nitrogen systems is well established, its direct application to realistic nitrogen rejection unit operating conditions is constrained by limited data within the relevant pressure–temperature ranges and by the absence of a unified framework that links freezing predictions to process simulation. Consequently, thermodynamic modeling and process simulation are often conducted independently, leaving operators without an integrated predictive tool to evaluate freezing risks under actual operating conditions.

This work addresses this gap by integrating rigorous thermodynamic solid–liquid–vapor equilibrium modeling with plant-scale process simulation for cryogenic methane–nitrogen systems. The novelty of the study lies in coupling Aspen HYSYS with ThermoFAST to enable simultaneous simulation of nitrogen rejection unit process performance and accurate prediction of freezing envelopes under industrial conditions. The primary objectives are to evaluate thermodynamic models for $\text{CH}_4\text{--N}_2$ solidification, to employ ThermoFAST for reliable estimation of solid–liquid–vapor equilibrium envelopes, and to identify freezing-prone process streams within a nitrogen rejection unit using Aspen HYSYS. By directly linking thermodynamic freezing predictions with process-level simulations, the proposed approach establishes a practical and predictive framework for anticipating solid formation, thereby enhancing safety, operability, and efficiency in cryogenic nitrogen rejection from natural gas.

2. Methodology

An integrated simulation workflow was implemented to evaluate phase behavior and freezing risk in $\text{CH}_4\text{--N}_2$ mixtures under cryogenic conditions. The workflow combines (i) steady-state process simulation in Aspen HYSYS and (ii) thermodynamic envelope analysis in ThermoFAST. Aspen HYSYS enables rigorous plant-scale modeling of cryogenic nitrogen rejection unit operations with robust convergence and validated property methods, thereby supporting realistic flowsheet development and comprehensive heat-integration studies. It provides accurate and stable representation of industrial-scale cryogenic processes and incorporates built-in tools for sensitivity analysis and process optimization (Ghasemzadeh et al., 2016; Jafari et al., 2019; Jafari et al., 2023). ThermoFAST delivers high-fidelity phase equilibrium and solid–liquid–vapor equilibrium envelope predictions using advanced equations of state and solid-phase models, enabling precise identification of solid-formation boundaries over broad temperature and pressure ranges (Yang et al., 2022). The combined approach facilitates the definition of safe operating windows and the mitigation of solid-formation risks in a representative nitrogen rejection unit.

It should be noted that Aspen HYSYS does not explicitly resolve solid–liquid–vapor equilibrium for $\text{CH}_4\text{--N}_2$ systems, and its treatment of the solid phase is largely limited to carbon dioxide freezing-point detection. Therefore, coupling Aspen HYSYS with ThermoFAST is necessary to extend the analysis to solid formation in methane–nitrogen mixtures and to ensure a physically consistent evaluation of freezing risk under cryogenic nitrogen rejection unit conditions. Within this integrated framework, freezing boundaries predicted near the eutectic region are interpreted conservatively, and appropriate operational safety margins are applied to account for model sensitivity and uncertainty.

2.1. Thermodynamic modeling and solid–liquid–vapor equilibrium envelope prediction for CH₄–N₂ mixtures

2.1.1. Thermodynamic model selection and formulation

The framework employs a Helmholtz-energy-based equation of state of the PC-SAFT family to describe the fluid phases, including both vapor and liquid, coupled with a pure-solid representation of the crystalline phases based on the Lennard-Jones Weeks–Chandler–Andersen model. In this formulation, the solid phases are assumed to be immiscible, with each solid phase consisting of a single pure component, either N₂(s) or CH₄(s). This approach ensures consistent calculation of component chemical potentials from a unified Helmholtz free-energy potential for all phases, which are subsequently used to enforce phase equilibrium conditions among vapor, liquid, and solid phases. All PC-SAFT pure-component parameters and solid-phase reference properties employed in this study were obtained directly from the ThermoFAST database and established literature sources. No additional parameter regression was conducted; model performance was evaluated exclusively through validation against independent experimental solid–liquid equilibrium data.

This methodology has been shown to accurately represent solid–fluid equilibria at low to moderate pressures and is well suited for constructing the solid–liquid–vapor pressure–temperature boundary relevant to cryogenic separation and freezing-risk assessment (Gross and Sadowski, 2001). Three-phase equilibrium is imposed by requiring equality of the chemical potential of each component across all coexisting phases. For a pure compound, Equation 1 expresses the solid–liquid–vapor equilibrium condition (Raposa et al., 2022).

$$\mu^V(T, P) = \mu^L(T, P) = \mu^S(T, P) \quad (1)$$

For a binary mixture, Equation 2 generalizes this condition by enforcing the equality of the chemical potentials of each component across the vapor, liquid, and solid phases, considering the appropriate phase compositions. According to the Gibbs phase rule, the CH₄–N₂ solid–liquid–vapor (SLV) line is univariant; once the equation of state (EOS) and the pure-solid reference states are specified, the three-phase pressure becomes a single-valued function of temperature, $P_{SLV} = P_{SLV}(T)$. For two-phase equilibria, such as vapor–liquid (VLE) or vapor–solid (VSE) equilibria, the same principle applies, but it is enforced only between the vapor phase and the relevant condensed phase (Raposa et al., 2022).

$$\mu_i^V(x^V, T, P) = \mu_i^L(x^L, T, P) = \mu_i^S(x^S, T, P) \quad (2)$$

In the Helmholtz formulation, the equation of state (EOS) provides explicit working expressions for the chemical potentials. Equation 3 expresses the chemical potential of component i in the vapor phase in terms of (i) an ideal contribution, including $RT \ln(x_i P)$; (ii) a residual Helmholtz term A^R and its composition derivatives, which account for non-ideality; and (iii) density-dependent terms that ensure thermodynamic consistency with the EOS pressure relation. For a pure compound, the corresponding expression is given directly by Equation 4. The logarithmic terms on the right-hand side of Equations 3 and 4 are linked to the EOS pressure expression in Equation 5, which relates pressure P , temperature T , and the phase density ρ . In practice, for a given T , P , and x , Equation 5 is solved for ρ in each phase, the chemical potential μ (or equivalently the fugacity) is evaluated, and the equalities in Equations 1 and 2 are enforced.

$$\begin{aligned} \mu_i^V(x^V, T, P) = & \Gamma_i(T) + RT \ln(x_i^V, P) + A^R + \left(\frac{\partial A^R}{\partial x_i^V} \right)_{T, \rho^V, x_{j \neq i}^V} + \sum x_j \left(\frac{\partial A^R}{\partial x_i^V} \right)_{T, \rho^V, x_{j \neq i}^V} \\ & + \rho^V \left(\frac{\partial A^R}{\partial \rho^V} \right)_{T, x^V} - RT \ln \left(1 + \frac{\rho^V}{RT} \left(\frac{\partial A^R}{\partial \rho^V} \right)_{T, x^V} \right) \end{aligned} \quad (3)$$

$$\mu^V(T, P) = \Gamma(T) + RT \ln(P) + A^R + \left(\frac{\partial A^R}{\partial \rho^V} \right)_T - RT \ln \left(1 + \frac{\rho^V}{RT} \left(\frac{\partial A^R}{\partial \rho^V} \right)_T \right) \quad (4)$$

$$\frac{P}{\rho^V RT} = 1 + \frac{\rho^V}{RT} \left(\frac{\partial A^R}{\partial \rho^V} \right)_{T, x^V} \quad (5)$$

To construct the SLV curve, temperature is employed as the marching parameter between the pure-component triple-point limits. At each temperature step, the unknowns are the three-phase pressure and the coexisting fluid-phase compositions, while the solids are assumed to be pure. The equilibrium problem is formulated in terms of the fugacity equalities $f_i^V = f_i^L = f_i^S$, where, for the fluid phases, $f_i^\alpha = \phi_i^\alpha x_i^\alpha P$ is obtained from the EOS, and for the solid phase, $f_i^S(T, P)$ is referenced to the triple point with a pressure correction applied via the solid molar volume (Tan and Kargel, 2018). A robust nonlinear solver, such as a Newton or trust-region method, is employed, with the converged solution at one temperature serving as the initial guess for the next step. The resulting converged pair (T, P_{SLV}) defines a point on the three-phase line; repeating this procedure produces a continuous pressure–temperature boundary suitable for freezing-risk screening in cryogenic units (Raposa et al., 2022).

Model parameters are organized as follows. First, pure-component fluid parameters for PC-SAFT, including the segment number m , segment diameter σ , dispersion energy ε/k , and association terms where applicable, are typically regressed to high-quality thermophysical data. Second, pure-solid reference states define the thermodynamic behavior of the solid phases. Third, binary interaction parameters (BIPs) adjust unlike interactions through the EOS mixing rules. In practice, fluid-phase BIPs are calibrated to mixture vapor–liquid equilibria (VLE), whereas liquidus (solid–liquid equilibrium, SLE) data constrain the solid-phase BIPs. Consequently, new liquidus or SLV measurements can be employed to validate, refine, or derive the solid-phase BIPs while keeping the fluid parameters fixed.

2.1.2. Numerical procedure and SLV envelope construction

The SLV boundary for CH₄–N₂ mixtures is computed using the Helmholtz-energy framework described above. Because the binary SLV line is univariant, temperature is employed as the continuation variable between the pure-component triple points. For each temperature T , the unknowns are the three-phase pressure P_{SLV} and the fluid-phase compositions x^V and x^L , while the solids are assumed to be pure.

At each step, the phase densities for vapor and liquid are obtained by solving the EOS pressure relation (Equation 5). Chemical potentials, or equivalently fugacities, are then calculated for all phases, and the equilibrium equalities in Equations 1 and 2 are enforced. The resulting nonlinear system is solved using a robust iterative method, such as a damped Newton or trust-region approach, with adaptive step control applied near turning points of the pressure–temperature curve or close to the pure-component bounds; pseudo-arclength continuation is employed when required.

Convergence is assessed using stringent residual tolerances, for example, $|\ln(f_i^\alpha/f_i^\beta)|$ in the range 10^{-8} – 10^{-6} and $\sum x_i^\alpha = 1$ within 10^{-10} . Each converged pair (T, P_{SLV}) defines a point on the SLV line.

Repeating this procedure generates a continuous $P_{\text{SLV}}(T)$ curve, with the neighboring two-phase edges (VLE or VSE) identified at points where the fraction of one condensed phase vanishes.

The final outputs include:

- The continuous SLV pressure–temperature relation $P_{\text{SLV}}(T)$
- Coexisting fluid compositions $x^V(T)$ and $x^L(T)$
- Auxiliary properties, such as densities and enthalpies, for process integration

These results provide a rigorous basis for freezing-risk screening and for quantifying operating margins ($\Delta T, \Delta P$) between actual process conditions and the SLV boundary in cryogenic units. The implementation strictly adheres to the assumptions of Section 2.1.1 and is presented as a descriptive methodology rather than as a novel model development.

2.1.3. Validation of ThermoFAST predictions against experimental data

The reliability of the ThermoFAST software in predicting the solid–liquid equilibrium (SLE) behavior of methane–nitrogen mixtures was assessed by comparing its predicted freezing points with experimental measurements across the full composition range (Table 1, Figure 1). Absolute and relative errors were computed for each composition, spanning CH_4 mole fractions from 0% to 100%. It is emphasized that this comparison represents a purely validation exercise, as all model parameters were fixed a priori and were not adjusted to fit the experimental data presented.

The results indicate that the absolute error remains below 7 K and the relative error below 11% for all compositions. The largest deviations occur between 10 and 21 mol% CH_4 , near the eutectic composition ($x_{\text{CH}_4} \approx 0.16$), where the freezing temperature reaches its minimum (~ 56 K) and both $\text{CH}_4(\text{s})$ and $\text{N}_2(\text{s})$ can coexist with the liquid phase. In this region, the SLE boundary is highly sensitive to the shape of the liquidus curve and to non-ideal molecular interactions, such that slight variations in model parameters can produce differences of several kelvins. Experimentally, this sensitivity is compounded by undercooling, delayed crystal nucleation, and the formation of fine solids that may be undetectable by visual or turbidity-based methods. Additional uncertainty of 5–7 K can arise from temperature gradients, high cooling rates, and sensor limitations under cryogenic conditions.

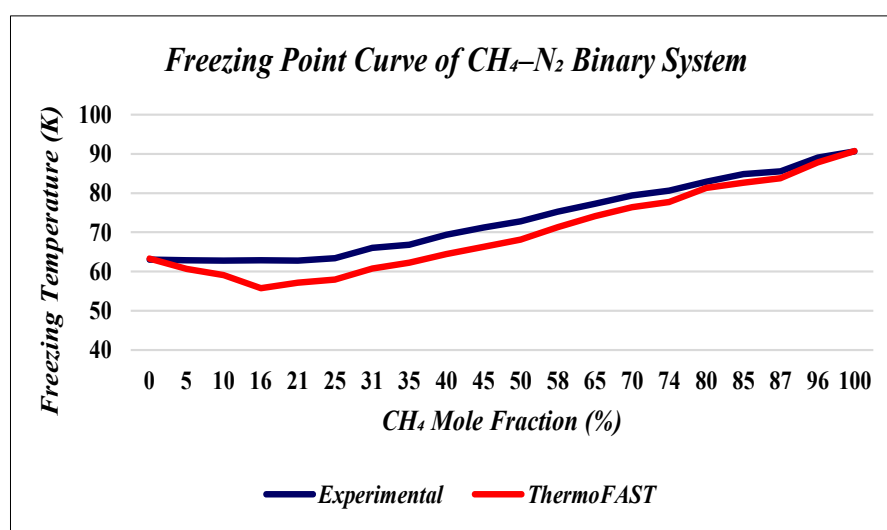


Figure 1

Comparison of freezing-point curves for $\text{CH}_4\text{--N}_2$ binary mixtures based on experimental data and ThermoFAST predictions

Despite this localized increase in error, ThermoFAST reproduces the overall freezing curve accurately, achieving exact agreement at the pure-component limits, which confirms the correctness of its pure-solid reference states. The average absolute error across all data points is 3.45 K, with a mean relative error of approximately 5%, a level of accuracy acceptable for early-stage process design, hazard screening, and evaluation of operational margins. By combining rigorous thermodynamic modeling with accurate solid-phase reference data, ThermoFAST provides rapid, consistent SLE predictions and reliably identifies high-risk regions for simultaneous solid-phase formation—an essential capability for LNG production, nitrogen rejection, and other cryogenic separation processes.

Table 1

Absolute and relative errors between experimental and ThermoFAST-predicted freezing points of CH₄–N₂ mixtures

CH ₄ mole %	Experimental	ThermoFAST	Absolute error	Relative error (%)
0	63	63	0	0
5	63	61	2	3
10	63	59	4	6
16	63	56	7	11
21	63	57	6	10
25	63	58	5	8
31	66	61	5	8
35	67	62	5	7
40	69	64	5	7
45	71	66	5	7
50	73	68	5	7
58	75	71	4	5
65	77	74	3	4
70	79	76	3	4
74	81	78	3	4
80	83	81	2	2
85	85	83	2	2
87	86	84	2	2
96	89	88	1	1
100	91	91	0	0

2.2. Aspen HYSYS process simulation

The cryogenic separation process was simulated using Aspen HYSYS v14 under steady-state conditions. The configuration represents a simplified nitrogen-rejection unit (NRU) commonly employed in natural gas processing and helium recovery facilities. The Peng–Robinson (PR) equation of state was selected as the primary thermodynamic model because of its reliability in representing non-ideal gas behavior, particularly at the low temperatures and high pressures characteristic of cryogenic operations. The feed gas consisted of a binary methane–nitrogen mixture introduced into the separation system in a fully vaporized state. The chosen process conditions correspond to standard upstream specifications for natural gas prior to cryogenic treatment. Detailed thermodynamic and compositional

properties of the feed are provided in Table 2. This composition reflects a low-nitrogen natural gas stream, which is typically targeted in NRU applications.

The NRU was modeled using a single-column design, inspired by the configuration reported by Rufford et al. (2012). The separation process comprises a sequence of pre-cooling, expansion, and low-temperature distillation steps, which are designed to selectively remove nitrogen via cryogenic rectification. The process begins with the feed gas entering the cryogenic section, where it is gradually cooled through heat exchange with returning cold streams and an external refrigeration cycle. Upon reaching cryogenic temperatures, the gas is expanded to promote partial condensation, forming a two-phase mixture of vapor and liquid.

Table 2
Feed stream specifications used in Aspen HYSYS simulation

Stream name	NG (feed)
Temperature [K]	298.15
Pressure [kPa]	6000
Molar flow [kgmole/h]	52620
Mass flow [kg/h]	875671
N ₂ mole fraction	0.05
CH ₄ mole fraction	0.95

This two-phase stream is subsequently fed into a cryogenic distillation column, where separation is achieved based on differences in component volatility. Nitrogen, being the lighter and more volatile component, is withdrawn from the top of the column, while the methane-rich product, commonly referred to as sales gas, is recovered from the bottom. Additional refrigeration is provided through an external cooling loop, which includes compressors and heat exchangers to reduce the temperature of auxiliary nitrogen streams. Column performance is regulated by adjusting key operational parameters, such as the reflux ratio, reboiler duty, and column pressure. This configuration enables efficient nitrogen rejection and, depending on the feed composition, facilitates the recovery of helium as a valuable by-product. An overview of the simulated process is presented in Figure 2, which depicts the block flow diagram (BFD) and highlights the main stages of cryogenic nitrogen separation.

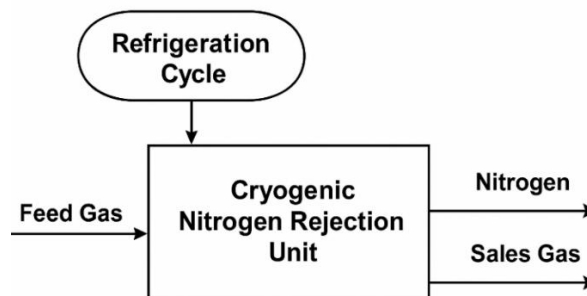


Figure 2

Block flow diagram of the cryogenic nitrogen rejection process from natural gas

3. Process simulation details

The cryogenic nitrogen rejection process simulated in Aspen HYSYS is designed to selectively separate nitrogen from a methane-rich natural gas stream using a combination of heat integration, Joule–

Thomson expansion, and cryogenic distillation. As shown in Figure 3, the process begins with the natural gas feed entering a multi-stream heat exchanger (MSHE-101), where it is progressively cooled against returning low-temperature product and waste streams. The feed gas enters at 298.15 K and 6.00 MPa, with a total mass flow rate of approximately 875,671 kg/h and a mole fraction of 95% methane and 5% nitrogen.

After pre-cooling, the feed stream undergoes isenthalpic expansion through an expander (K-101), reducing its temperature to approximately 167.15 K and partially condensing the gas mixture. This two-phase stream is then introduced into a cryogenic distillation column (T-101), which operates with 15 theoretical stages and a top-down stage numbering scheme. The column operates between a top pressure of 1.00 MPa and a bottom pressure of 1.20 MPa. The partially condensed feed enters the column at Stage 11, with additional inlets and side draws incorporated to provide operational flexibility.

Separation within the column is driven by the volatility difference between methane and nitrogen. Nitrogen, being more volatile, rises through the column and exits as a high-purity vapor stream at 114.15 K and 1.00 MPa. The methane-rich product is withdrawn from the bottom at 152.59 K and 1.20 MPa, with a CH₄ mole fraction approaching 100%. An external refrigeration cycle, consisting of two compressors (K-102 and K-103), a cooling water exchanger (CW-101), and an auxiliary nitrogen stream, supplies additional cooling to maintain cryogenic temperatures. Multiple heat exchangers recover and integrate cold energy throughout the cycle, enhancing thermal efficiency.

Pressure control and product quality are maintained using control valves (VLV-100, VLV-101, VLV-102) and strategically placed side streams. Reflux and reboiler duties are adjusted to optimize separation while minimizing methane losses to the nitrogen-rich overhead stream. The simulation monitors thermodynamic variables and compositions at each stage, enabling direct integration with ThermoFAST for freezing-risk assessment.

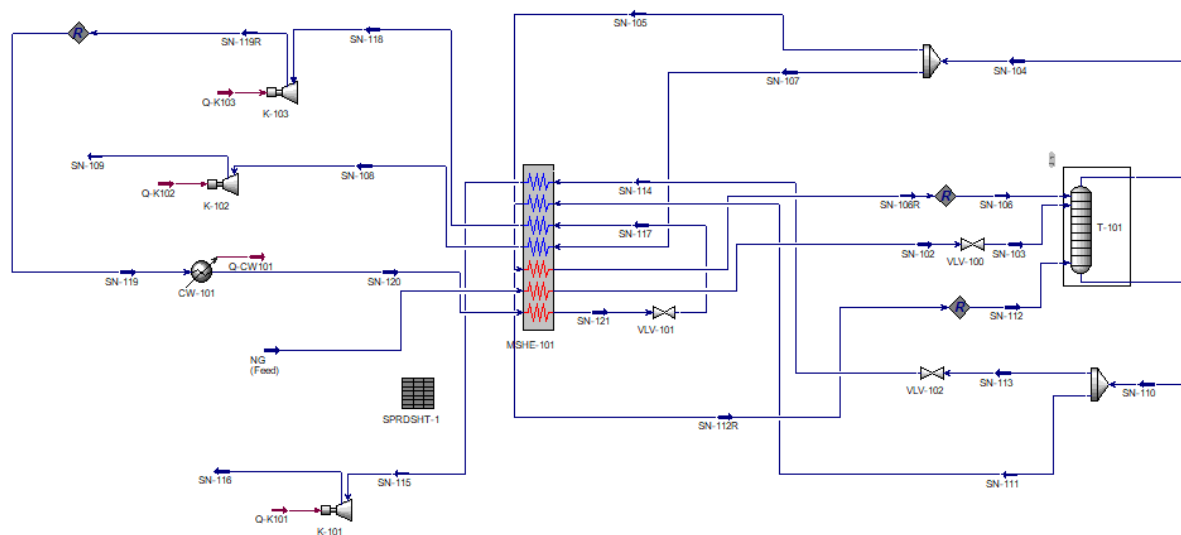


Figure 3

Aspen HYSYS-based simulation of a single-column cryogenic nitrogen rejection process for methane–nitrogen mixtures

4. Results and discussion

Figure 4 summarizes the key operating parameters obtained from the Aspen HYSYS simulation of the single-column cryogenic nitrogen rejection process for methane–nitrogen mixtures. The process requires a total power input of 291 MW, primarily associated with gas compression, refrigeration, and

pumping duties necessary to achieve the sub-ambient temperatures required for phase separation. Cooling water consumption is 122 t/h, reflecting the thermal load in the process heat exchangers. The total feed to the column is 876 t/h of natural gas, from which 801 t/h of high-purity methane is recovered as the primary product stream. These results demonstrate that the process achieves a high methane recovery yield while maintaining stable energy and cooling demands, in line with the design objectives of maximizing methane purity and minimizing nitrogen content in the product stream.

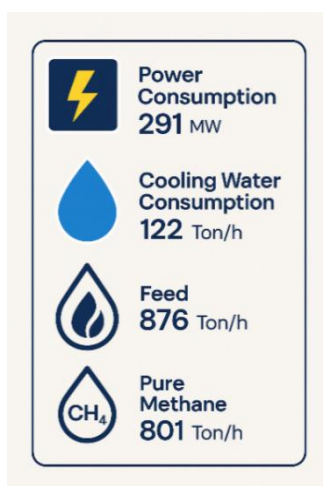


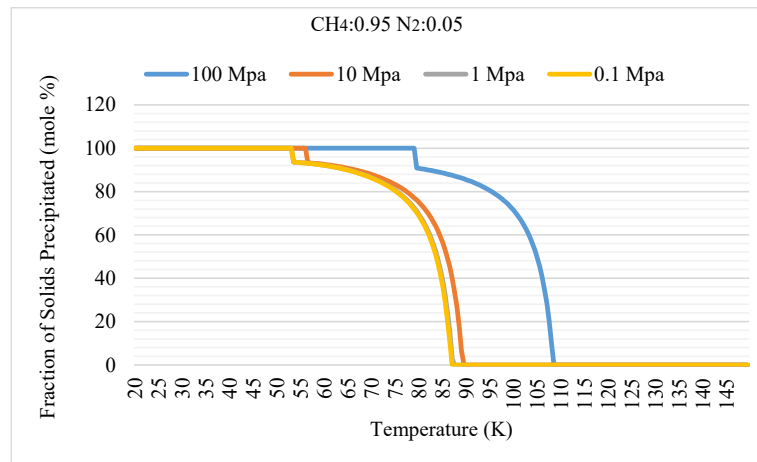
Figure 4

Key operating parameters from Aspen HYSYS simulation of the single-column cryogenic nitrogen rejection process

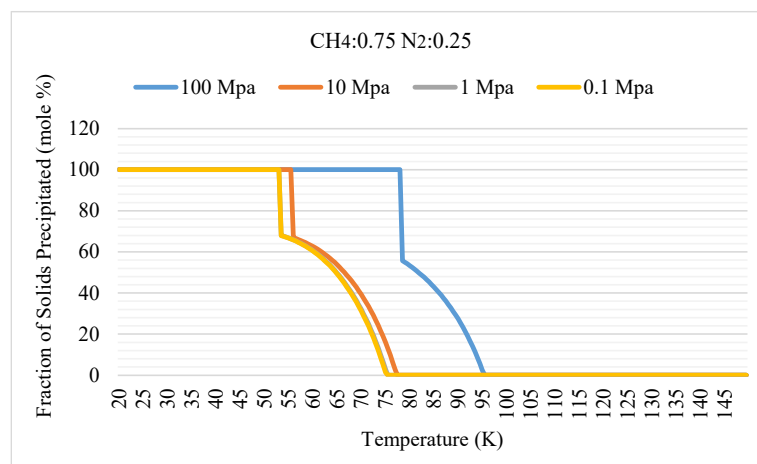
Figures 5–8 illustrate the variation in the fraction of solids precipitated for $\text{CH}_4\text{--N}_2$ mixtures at four pressures (0.1, 1, 10, and 100 MPa) and compositions ranging from methane-rich to nitrogen-rich. For the CH_4 -rich mixture (CH_4 0.95 – N_2 0.05, Figure 5), the solid phase is dominated by $\text{CH}_4(\text{s})$, resulting in high solid fractions that remain nearly constant over a broad temperature range before a sharp decline occurs near the CH_4 melting temperature. At low pressures (0.1–1 MPa), this decline is steep and narrow, characteristic of eutectic behavior controlled by $\text{CH}_4(\text{s})$ melting. Increasing the pressure from 10 to 100 MPa shifts the onset of melting to higher temperatures and broadens the transition region, indicating enhanced thermodynamic stability of the solid phase under elevated pressures.

Reducing the methane content to CH_4 0.75 – N_2 0.25 (Figure 6) leads to a pronounced depression of the eutectic temperature, with all curves shifting to lower temperatures compared to the methane-rich case. The low-pressure curves (0.1–1 MPa) exhibit an earlier decline in solid fraction, whereas at high pressures the shift toward warmer melting onset persists. The high-solid plateau becomes shorter, and the melting transition becomes steeper, suggesting that the addition of nitrogen destabilizes $\text{CH}_4(\text{s})$ and increases the sensitivity of the eutectic point to composition changes.

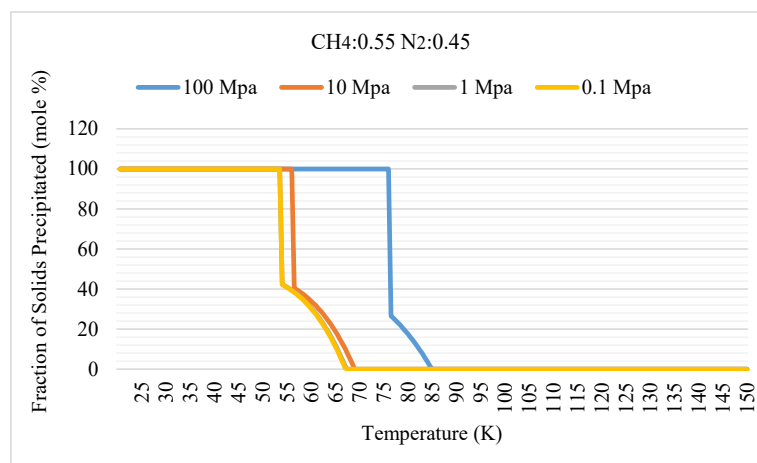
For intermediate and nitrogen-rich mixtures (CH_4 0.55 – N_2 0.45, Figure 7; CH_4 0.35 – N_2 0.65, Figure 8), the onset of melting occurs at progressively lower temperatures. At low pressures, solids disappear at significantly colder temperatures, and even at high pressures, the high-solid plateau is brief. The controlling solid phase gradually transitions from $\text{CH}_4(\text{s})$ to $\text{N}_2(\text{s})$, with the melting-point shift approaching the nitrogen freezing point. While increasing pressure still raises the eutectic temperature in all cases, its relative effect diminishes with higher nitrogen content due to the inherently lower melting point of $\text{N}_2(\text{s})$.

**Figure 5**

Fraction of solids precipitated versus temperature at various pressures: ThermoFAST results for CH₄ (0.95)–N₂ (0.05) mixture

**Figure 6**

Fraction of solids precipitated versus temperature at various pressures: ThermoFAST results for CH₄ (0.75)–N₂ (0.25) mixture

**Figure 7**

Fraction of solids precipitated versus temperature at various pressures: ThermoFAST results for CH₄ (0.55)–N₂ (0.45) mixture

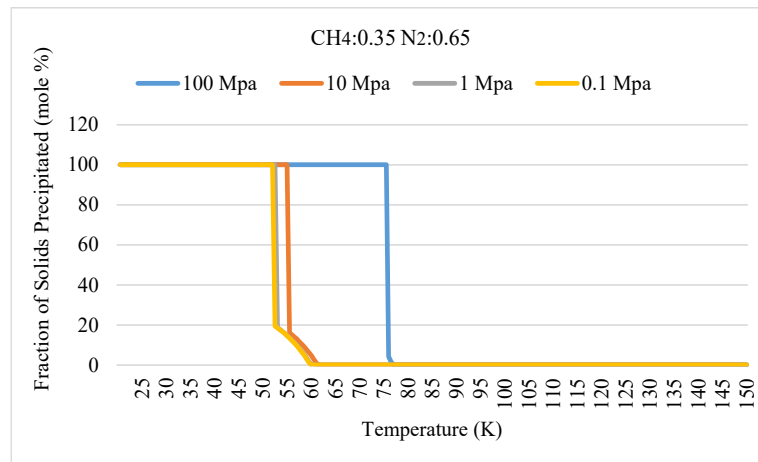


Figure 8

Fraction of solids precipitated versus temperature at various pressures: ThermoFAST results for CH₄ (0.35)–N₂ (0.65) mixture

Overall, the results indicate that increasing pressure consistently raises the eutectic temperature and broadens the stability range of the solid phase. In contrast, higher nitrogen content depresses the eutectic temperature and reduces the temperature interval over which solids persist. From a process safety and operability perspective, solid formation is most likely in methane-rich streams (CH₄ $\geq$ 0.75) at high pressures ($\geq$ 10 MPa), where solids can precipitate at relatively warm cryogenic temperatures. Conversely, nitrogen-rich mixtures (CH₄ $\leq$ 0.55) require substantially lower temperatures—particularly under low-pressure conditions—before solid formation becomes significant.

Figure 9 presents the model-only pressure–temperature (P – T) three-phase (SLV) boundary for the N₂/CH₄ binary system, delineating conditions under which solid, liquid, and vapor coexist for specific compositions. The curve connects the approximate triple points of N₂ (~63 K) and CH₄ (~90 K) and exhibits an S-shaped profile with a mid-temperature pressure maximum (schematically ~0.6–0.7 bar near 78–80 K). This behavior indicates that three-phase equilibrium occurs at very low pressures near the pure-component triple points but requires higher pressure at intermediate temperatures.

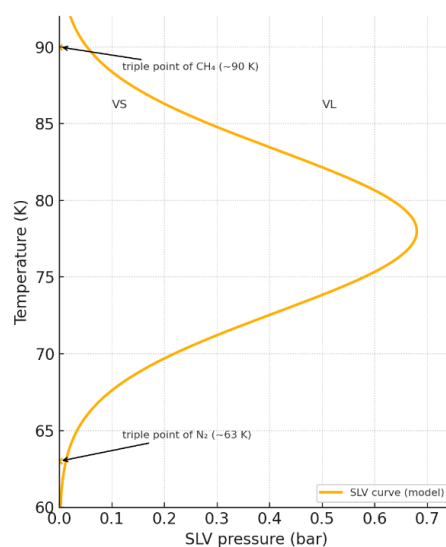


Figure 9

Model-only SLV pressure–temperature envelope for the N₂/CH₄ binary, indicating approximate triple points and adjacent VL/VS regions

Regions adjacent to the boundary are labeled VL (vapor–liquid) and VS (vapor–solid), with crossing toward the VS region signaling the onset of solid formation. Operationally, NRU process paths that approach this boundary—after Joule–Thomson expansion, within cold heat-exchanger passes, or on upper column trays—face elevated freezing risk. Maintaining a 2–3 K temperature margin and controlling pressure drops are effective measures to avoid entry into the VS domain. Because this is a P – T projection of the (P, T, x) space, each point corresponds to a specific composition; rigorous freezing-risk screening should therefore combine this envelope with ThermoFAST-derived compositions and Aspen HYSYS process profiles. Numerical values shown are schematic and can be refined using calibrated model parameters or case-specific data.

The thermodynamic behavior of key process streams within the cryogenic separation unit was examined to identify potential freezing risks under operational conditions. Relevant data, summarized in Table 3, include vapor fraction, temperature, pressure, flow rate, composition, and calculated freezing point for each stream. Freezing points were determined based on mole-fraction-dependent solid–liquid equilibrium modeling using ThermoFAST. A clear trend is observed between the mole fractions of nitrogen and methane and the corresponding freezing-point temperatures. Nitrogen-rich streams, such as SN-104 to SN-109, with nitrogen mole fractions around 90%, exhibit significantly lower freezing points near 84.15 K. These values are consistent with the known SLE behavior of the CH_4 – N_2 binary system, where increasing nitrogen content causes a marked depression of the freezing point due to nitrogen's inherently lower triple-point temperature.

In contrast, streams composed entirely of methane (e.g., SN-110 to SN-121, 100% CH_4) exhibit higher freezing points, ranging from 90.65 K to 91.25 K. These variations are primarily due to differences in pressure and phase (vapor versus liquid) across process locations. For instance, SN-114, operating at a very low pressure of 0.05 MPa, is more susceptible to freezing because of reduced thermal buffering and lower enthalpy. Similarly, SN-106 (105.15 K, liquid phase, 0.98 MPa) is positioned near the nitrogen-rich freezing zone, representing a potential risk point for solid formation if temperature fluctuations occur. Conversely, several methane-rich streams, including SN-115 and SN-116, operate at temperatures well above the freezing region, making them thermodynamically stable. Reheated or compressed streams (e.g., SN-119 and SN-120) also remain outside the critical freezing window, highlighting the effectiveness of operational heating in post-separation stages.

A notable case is SN-117, a mixed-phase stream with a vapor fraction of 0.12 and a temperature of 111.40 K. Despite being pure methane, its proximity to the freezing point (90.65 K) underscores the importance of phase and pressure in determining the location of the solid–liquid boundary. This example illustrates that even single-component streams can approach freezing if operated near the triple point.

From a design and safety perspective, the most critical zones are the coldest stages immediately following expansion and separation (e.g., SN-104 to SN-108), where nitrogen enrichment and extreme subcooling coincide. Effective insulation, precise control of Joule–Thomson expansion, and localized heating are essential to prevent accidental solidification and blockages. Table 3 therefore highlights a thermodynamic landscape in which freezing risks are not uniformly distributed but depend on both composition and location within the process. Integrating freezing-point calculations into the simulation workflow provides a robust framework for identifying vulnerable points and proactively addressing phase-change hazards during cryogenic separation.

Table 3
Process stream conditions and freezing-point risk assessment across the cryogenic separation unit

	Vapor fraction	Temperature (K)	Pressure (MPa)	Mass flow (kg/h)	N ₂ , mole%	CH ₄ , mole%	Freezing point (K)
NG (Feed)	1.00	298.15	6.00	875670.74	0.05	0.95	88.56
SN-102	0.00	169.11	5.98	875670.74	0.05	0.95	88.55
SN-103	0.00	167.1	2.89	875670.74	0.05	0.95	87.82
SN-104	1.00	113.76	1.00	934000.14	0.90	0.10	84.08
SN-105	1.00	113.76	1.00	858714.26	0.90	0.10	84.08
SN-106	0.00	105.15	0.98	858747.90	0.90	0.10	84.08
SN-107	1.00	113.76	1.00	75285.88	0.90	0.10	84.08
SN-108	1.00	289.88	0.98	75285.88	0.90	0.10	84.08
SN-109	1.00	448.71	3.45	75285.88	0.90	0.10	84.66
SN-110	0.00	152.59	1.20	1047947.32	0.00	1.00	90.94
SN-111	0.00	152.59	1.20	247353.53	0.00	1.00	90.94
SN-112	1.00	152.75	1.18	247528.82	0.00	1.00	90.93
SN-113	0.00	152.59	1.20	800593.79	0.00	1.00	90.94
SN-114	0.36	102.48	0.05	800593.79	0.00	1.00	90.96
SN-115	1.00	268.15	0.03	800593.79	0.00	1.00	90.66
SN-116	1.00	717.19	1.83	800593.79	0.00	1.00	91.09
SN-117	0.12	111.4	0.10	2887.72	0.00	1.00	90.67
SN-118	1.00	293.15	0.10	2887.72	0.00	1.00	90.67
SN-119	1.00	616.64	2.19	2887.72	0.00	1.00	91.18
SN-120	1.00	303.15	2.17	2887.72	0.00	1.00	91.17
SN-121	0.00	128.2	2.15	2887.72	0.00	1.00	91.17

Operationally, the freezing envelopes calculated in this study can serve as practical operating limits for NRU units. During routine operation, these limits are applied by maintaining a conservative temperature margin above the predicted freezing onset at the relevant pressure and nitrogen composition, enabling operators to define safe operating windows and alarm thresholds for critical cryogenic streams. Because key variables such as temperature, pressure, and nitrogen content are continuously monitored, these limits can be enforced without additional instrumentation, allowing timely corrective actions to reduce freezing risk. It should be noted, however, that while SLV results indicate thermodynamically favorable conditions for solid formation, actual plugging is also influenced by hydrodynamic and transport-related factors beyond equilibrium conditions.

5. Conclusions and future work

This study presented an integrated Aspen HYSYS–ThermoFAST framework for assessing and mitigating freezing hazards in cryogenic nitrogen rejection from methane-rich natural gas. Using the PC-SAFT equation of state for fluid phases and pure-solid reference data for CH₄ and N₂, the model accurately reproduced experimental freezing behavior, achieving a mean absolute error of 3.45 K and a mean relative error of approximately 5%, thereby providing a robust foundation for early-stage design

screening. Importantly, this level of agreement with experimental data was obtained without any parameter tuning, highlighting the predictive capability of the adopted thermodynamic framework.

Mapping process conditions onto SLV pressure–temperature envelopes revealed that freezing is most likely in methane-rich streams at approximately 91.15 K and in nitrogen-rich streams near 84.15 K, particularly following Joule–Thomson expansion, within cold heat-exchanger passes, and on upper column trays. Elevated pressures increase the eutectic temperature and expand the solid-phase stability range, whereas higher nitrogen content depresses the eutectic temperature and narrows the solid stability interval.

The proposed approach provides a transferable tool for defining safe operating windows in NRU operations and other cryogenic separations, including helium recovery and LNG polishing. Future work should focus on refining PC-SAFT parameters across mid-composition ranges, investigating non-ideal solid-solution effects, and extending the model to multicomponent mixtures containing CO₂, C₂H₆, heavier hydrocarbons, and He. Incorporating process dynamics, kinetic modeling, and computational fluid dynamics (CFD) will further enhance predictions of blockage onset, while advanced monitoring and control strategies can maintain safe temperature margins and improve operational reliability in high-risk cryogenic systems.

Nomenclature

BFD	Block flow diagram
BIP(s)	Binary interaction parameter(s)
CFD	Computational fluid dynamics
EOS	Equation of state
LJ	Lennard–Jones
LNG	Liquefied natural gas
MSHE	Multi-stream heat exchanger
NG	Natural gas
NRU	Nitrogen rejection unit
PC-SAFT	Perturbed-chain statistical associating fluid theory
PR	Peng–Robinson
SLE	Solid–liquid equilibrium
SLV	Solid–liquid–vapor
SLVE	Solid–liquid–vapor equilibrium
VL	Vapor–liquid
VLE	Vapor–liquid equilibrium
VS	Vapor–solid
VSE	Vapor–solid equilibrium
WCA	Weeks–Chandler–Andersen

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