

Gas-Liquid-Solid Multiphase Flow and Phase-Transition Mechanisms of Cryogenic CH₄-CO₂ Systems in Pipelines

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Abstract

CH₄-CO₂ mixtures are widely encountered in LNG liquefaction, CCUS transportation, cryogenic biogas upgrading, cryogenic carbon capture, and the reinjection of CO₂-rich associated gas. Low temperatures or rapid depressurization can bring the system close to the solid-CO₂ formation boundary, thereby triggering dry-ice crystallization and desublimation, particle agglomeration, and pipeline blockage. Based on the original review, this paper condenses the literature discussion while retaining five central themes: thermodynamic phase equilibrium, solid-phase nucleation, in-pipe multiphase flow, coupled heat and mass transfer, and numerical modeling. The results show that phase boundaries shift significantly with pressure, composition, and impurities; heterogeneous nucleation is more likely to dominate wall-frost formation; deposition and re-entrainment of dry-ice particles govern pressure-drop and heat-transfer risks; and engineering models require a coordinated choice between EOS thermophysical-property accuracy and CFD capability for resolving phase interfaces.

Keywords

Cryogenic Multiphase Flow; CH₄-CO₂ Binary System; Dry-Ice Particles; Phase-Transition Kinetics; Thermodynamic Nonequilibrium

1. Introduction

Expansion of LNG and CCUS infrastructure has made cryogenic CH₄-CO₂ flow assurance a practical design problem. Cooling or depressurization can cross vapor-liquid-solid boundaries, generating liquid condensation, CO₂ frost, dry-ice transport, deposition, and blockage. This review addresses fully dehydrated mixtures and connects phase equilibrium, nucleation, particle transport, heat and mass transfer, modeling, and monitoring to engineering operating envelopes.

2. Fundamentals of Cryogenic CH₄-CO₂ Systems

2.1. Phase Boundaries and the Engineering Operating Window

Phase boundaries depend strongly on pressure, composition, and the operating path (Figure 1). Experiments established critical and three-phase loci, including a pressure maximum, while later work extended data from LNG-like low- CO_2 mixtures to CO_2 -rich CCUS conditions and near-critical states. Cubic equations of state often capture vapor-liquid equilibrium but may mispredict solid formation, especially when binary interaction parameters are transferred beyond their fitted range. Consequently, freezing risk must be screened with a validated phase envelope and transient trajectory rather than a single temperature limit.

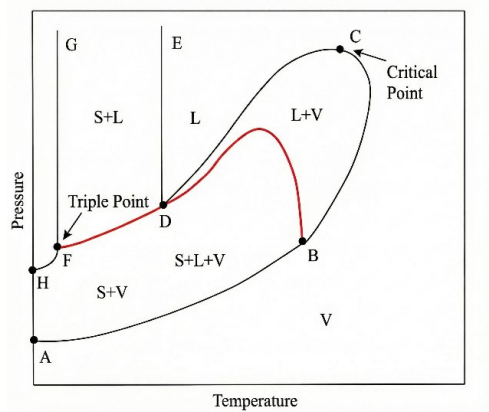


Figure 1. Phase diagram and representative phase regions of the CO_2 - CH_4 system

2.2. Crystallization, Desublimation, and Nucleation Mechanisms

Solid CO_2 forms by crystallization from a liquid-rich phase or by desublimation from gas. Crystallization produces suspended or wall-attached particles as solubility falls; desublimation deposits porous frost when gas becomes supersaturated. Péclet number and wall subcooling govern whether diffusion, convection, or interfacial kinetics controls the morphology (Figure 2). Homogeneous nucleation requires high supersaturation, whereas heterogeneous nucleation on rough walls, packings, or impurities lowers the barrier and usually determines the location of pipeline frost (Figure 3). Surface condition, contact angle, temperature gradient, and residence time are therefore central plugging variables.

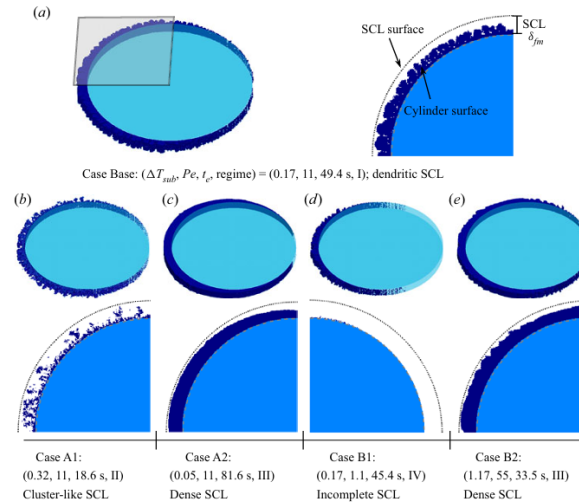


Figure 2. Three-dimensional CO₂ desublimation morphologies and the corresponding control regimes

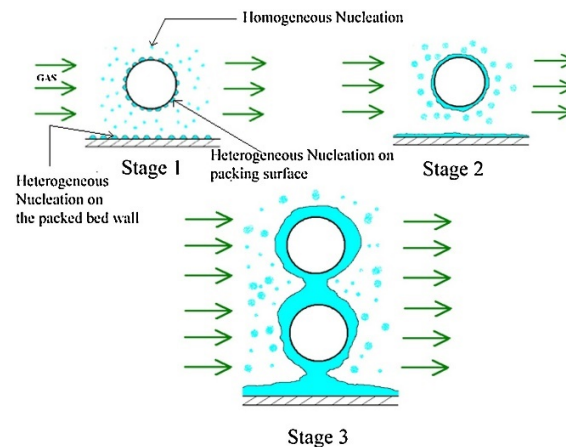


Figure 3. Schematic of heterogeneous nucleation on wall/packing surfaces and homogeneous nucleation within pores

3. In-Pipe Multiphase Flow and Particle Transport

Evidence comes from horizontal and vertical loops, blowdown systems, and industrial comparisons. Attenuation methods quantify phase distribution in opaque high-pressure flow, while fast pressure, temperature, and heat-flux sensors resolve transients. Horizontal loops emphasize holdup and pressure drop; vertical tests show slip and downward liquid accumulation; blowdown rigs capture rapid cooling and dry-ice formation. Once formed, particles deposit, agglomerate, fragment, and re-entrain rather than simply follow the carrier. Jet tests show that median size varies with nozzle diameter and downstream distance (Figure 4); low velocity and large passages favor deposition and a sharp pressure-drop rise.

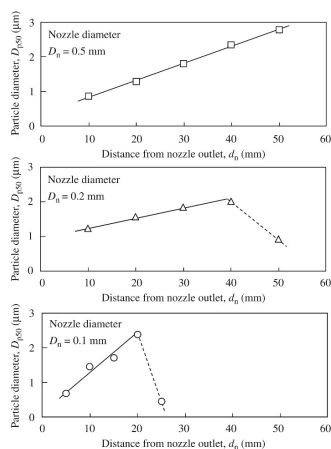


Figure 4. Effects of nozzle diameter and distance from the nozzle outlet on median dry-ice particle size

4. Phase-Transition Mechanisms and Coupled Effects

The flow couples thermodynamics, heat transfer, mass transfer, nucleation, and particle dynamics. Greater flow and vapor quality can enhance convection, whereas frost adds thermal resistance. Latent heat shifts the expansion path, and cryogenic diffusivity may fall enough to create diffusion freeze-out. Particles can improve mixing when dispersed but degrade heat transfer and constrict area after agglomeration or deposition. Because these feedbacks alter local supersaturation and pressure drop, phase change cannot be represented by an isothermal equilibrium switch alone.

5. Modeling and Numerical-Simulation Methods

Reliable simulation begins with thermophysical properties. PR and SRK equations are common, but frost-point accuracy depends strongly on the treatment of the binary interaction parameter; temperature-dependent forms usually outperform constants (Figure 5). For engineering pressure drop, holdup, and plugging boundaries, Eulerian–Eulerian models offer robust scale-up. Eulerian–Lagrangian or hybrid approaches better resolve dilute particles, trajectories, deposition, and re-entrainment at higher cost. Phase-field and molecular methods address nucleation physics, while machine learning can supply fast surrogates only within validated domains. A hierarchical workflow should couple EOS screening, local nonequilibrium phase change, and network-scale transport.

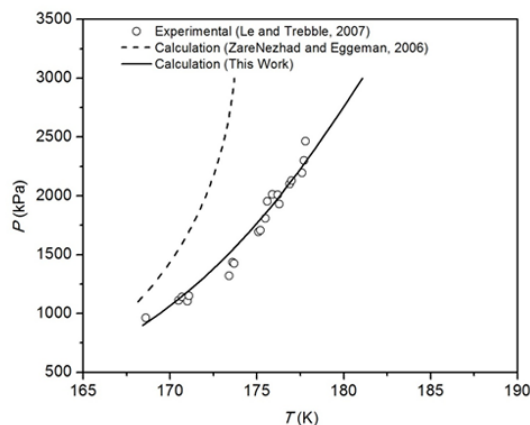


Figure 5. Comparison of frost-point calculations with experimental data under different treatments of k_{ij}

6. Conclusions and Outlook

The solid boundary varies with pressure, composition, impurities, and path; heterogeneous nucleation on cold surfaces is usually decisive. Although some CO_2 two-phase flows become nearly homogeneous, large diameters, downward flow, and rapid depressurization intensify segregation and deposition. Dispersed dry ice may enhance mixing, but agglomerated deposits add resistance and promote blockage. Coordinated EOS and multiphase CFD models are therefore required, supported by deeper-cryogenic equilibrium data, high-pressure visualization, and nonequilibrium validation.

7. Engineering Implications

In engineering applications, exclusion zones for cryogenic $\text{CH}_4\text{--CO}_2$ pipelines should not be based solely on steady-state phase diagrams; the risk window should also encompass startup, shutdown, blowdown, throttling, and heat-load fluctuations. For LNG systems, priorities include controlling the CO_2 content of the feed gas, maintaining an adequate cold-end temperature margin in the main cryogenic heat exchanger, and managing local stagnant zones. For CCUS networks, the priority is to identify the minimum-temperature location during rapid pressure reduction and the potential locations of dry-ice precipitation.

Monitoring should move from a single pressure or temperature threshold to multiparameter joint assessment. Pressure fluctuations, decreasing wall temperature, anomalous local pressure drop, and declining heat-exchange efficiency can jointly indicate frost growth or particle-bed formation. If the system has an adjustable heat source, localized thermal management should be prioritized at high-risk locations such as throttling devices, elbows, low points, and heat-exchanger inlets to reduce the probability of heterogeneous nucleation.

For model implementation, a hierarchical workflow of “phase-state screening–local

phase transition–network-wide transport” can be used. A corrected EOS first screens for solid-phase risk; nonequilibrium nucleation and heat–mass-coupled models are then introduced in critical pipe sections; finally, deposition–re-entrainment parameters are fed back into network pressure-drop calculations. This workflow retains computational efficiency for engineering applications while preventing purely empirical models from underestimating blockage-onset conditions.

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