



Coupled Thermodynamic Analysis of Hydrogen Refueling Station Storage Systems: Adiabatic Blowdown Dynamics and Compressor Charging Performance for H35 and H70 Infrastructure

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Abstract

Hydrogen refueling stations (HRS) require rigorous thermodynamic control during high-pressure dispensing (blowdown) and buffer storage replenishment (charging). This study presents complementary 0-D lumped-parameter models: an ideal-gas discharge model and a real-gas charging model using CoolProp for hydrogen behavior up to 100 MPa. Blowdown is analyzed for Type II (200 bar, 3.0 m³) and Type III (500 bar, 3.0 m³) vessels across three outflow profiles, while charging is evaluated for a 1.0 m³ buffer tank across H35 and H70 tiers at compressor flow rates of 0.005 and 0.01 kg/s. Results show that constant-rate discharge cools 200 bar tanks by 25–30 K over 300 s, compared to only 10–12 K for 500 bar tanks. Charging terminal states are flow-rate independent—doubling the flow rate halves duration without altering final conditions—while increasing initial mass inventory provides a pronounced thermal-buffering effect (e.g., raising m_0 from 40 to 45 kg in the H70 tier lowers peak temperature by 20 K, from 324.4 to 305.1 K). All scenarios comply with the 358.15 K (85°C) structural safety limit, maintaining a margin of at least 33.7 K. Overall, buffer tanks undergo severe cooling during discharge and moderate heating during charging, demonstrating that robust HRS control must jointly manage mass-based replenishment targets with explicit pressure ceilings.

Keywords: Hydrogen Refueling Stations (HRS), Type II and Type III Tanks, Adiabatic Blowdown, Compressor Charging, Real-Gas Thermodynamics, CoolProp, H35/H70 Infrastructure.

1. Introduction

Hydrogen is a high-density, zero-tailpipe-emission energy carrier central to the transition toward carbon-neutral mobility, produced from diverse renewable and low-carbon resources and yielding only water vapor when consumed in a fuel cell [1, 2]. Fuel-cell electric vehicles (FCEVs) combine internal-combustion-like range and refueling times (3–5 minutes) with electric-drivetrain efficiency, and major manufacturers – Toyota, Honda, Hyundai, and BMW – have brought FCEVs to market on this basis.

Hydrogen has the highest gravimetric energy density of any chemical fuel (≈ 120 MJ/kg, roughly triple gasoline), but its low volumetric density at standard conditions (0.089 kg/m³) demands densification. Cryogenic liquefaction, though thermodynamically attractive, incurs a significant energy penalty ($\approx 30\%$ of the lower heating value) and boil-off losses, so the industry has instead standardized on compressed gaseous storage at 35–70 MPa for FCEV refueling.

This has driven rapid growth in Hydrogen Refueling Station (HRS) infrastructure: by 2023, roughly 79,000 FCEVs were supported by more than 1,100 HRS worldwide – a 60% increase over two years [3]. Deployment is concentrated in Asia (China and South Korea each exceed 350 stations, Japan over 160), followed by Europe (around 240 stations, led by Germany, France, and the Netherlands), with North America expanding more gradually, led by California.

An HRS interfaces the hydrogen supply chain with the vehicle, typically comprising a hydrogen source (tube trailer, pipeline, or on-site electrolysis), multi-stage compression, a high-pressure Cascade Hydrogen Storage System (CHSS), a pre-cooling unit (chilling gas to $\approx -40^\circ\text{C}$ before dispensing), and a metering dispenser with breakaway couplings and leak detection.

The CHSS segments storage into low-, medium-, and high-pressure banks so the station–vehicle pressure differential can be exploited during dispensing, reducing compressor reliance and improving fill efficiency.

Station buffer tanks thus undergo two opposing, cyclically repeating loading events: (i) rapid adiabatic *blowdown* during vehicle transfer, where expansion cooling (the reverse Joule–Thomson effect) can drive temperatures sharply down and collapse pressure faster than mass depletion alone predicts; and (ii) subsequent compressor *charging*, where the enthalpy of incoming high-pressure gas raises the stored inventory’s internal energy and temperature. While vehicle-side fueling under protocols such as SAE J2601 is well studied, the coupled discharge–recharge dynamics of station-side buffer inventory have received little quantitative treatment, and most station-level studies assume a fixed final storage pressure, limiting applicability to real, variable operating conditions.

This work addresses that gap through two complementary zero-dimensional (0-D) thermodynamic analyses of station buffer storage:

1. **Discharge dynamics.** An ideal-gas adiabatic blowdown model simulates rapid depressurization of Type II (200 bar) and Type III (500 bar) buffer tanks under constant, pressure-dependent (decaying), and increasing outflow profiles, quantifying expansion cooling and pressure collapse.
2. **Charging dynamics.** A real-gas (CoolProp-based) adiabatic charging model simulates compressor recharging of 1.0 m³ buffer vessels in the H35 and H70 tiers, quantifying the sensitivity of charging duration, terminal pressure, and peak gas temperature to compressor mass flow rate and initial mass inventory.

Together, these analyses characterize the full thermodynamic duty cycle – cooling on discharge, heating on recharge – experienced by station storage infrastructure, translating into concrete design and control recommendations for HRS operators.

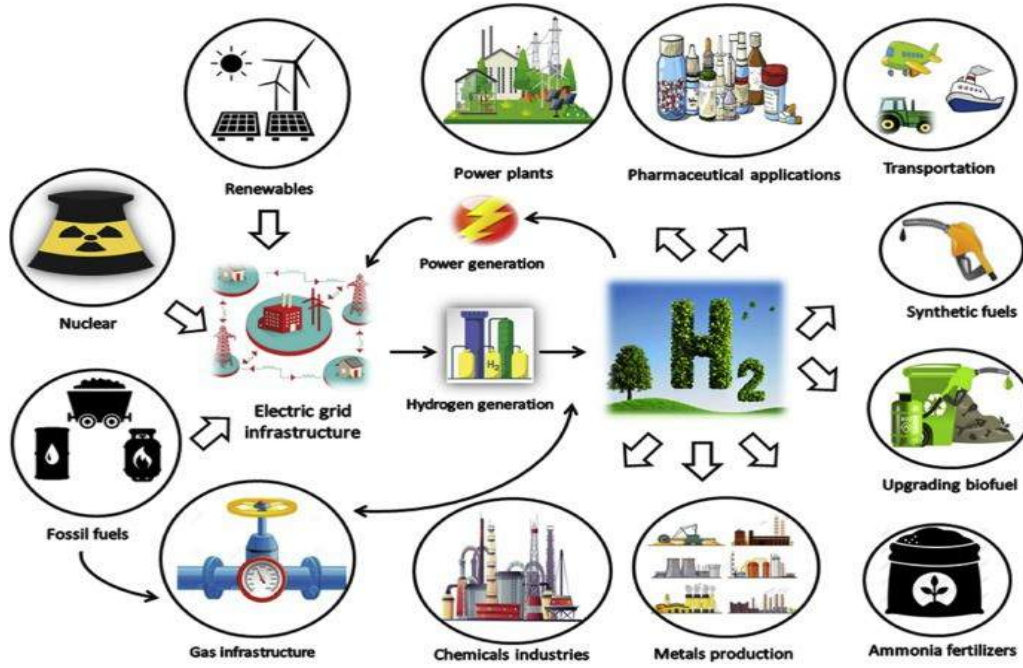


Figure 1: Overview of hydrogen production pathways and downstream applications: power, industry, transport, synthetic fuels, and biofuel upgrading [4].

2. Literature Review

2.1. Hydrogen as an Energy Storage Medium

Beyond transportation, hydrogen is increasingly recognized as a versatile energy-storage vector that decouples renewable generation from demand. Unlike batteries, whose cost scales with the electrochemical stack, hydrogen storage cost scales mainly with vessel or cavity size, making it well suited to long-duration and seasonal storage [5]. In a power-to-gas-to-power (P2G2P) pathway, surplus renewable electricity is electrolyzed to hydrogen, stored, and later reconverted via fuel cells or turbines, or alternatively injected into the gas grid, used as feedstock, or dispensed to FCEVs – the station infrastructure studied here is thus one terminal node of a broader hydrogen storage-and-distribution system [6].

Large-scale storage falls into three categories: (i) geological storage (salt caverns, depleted reservoirs, aquifers) – hundreds of GWh capacity at low specific cost, but geology-constrained; (ii) compressed gaseous storage in engineered vessels (Type I–IV, Section 2.3) – high round-trip efficiency and fast response at higher capital cost; and (iii) liquid hydrogen (LH2) – highest volumetric density but with a ~30% liquefaction energy penalty and continuous boil-off [5, 6, 7]. Compressed gaseous storage, the focus of this study, dominates HRS buffer/cascade applications for its rapid cycling and low parasitic losses, at the cost of lower volumetric density than the alternatives.

Metal/complex hydrides offer an alternative solid-state pathway, storing hydrogen at near-ambient pressure via reversible bonding – higher volumetric density and improved safety than compressed gas, but with added mass, slower kinetics, and (for complex hydrides) incomplete reversibility or high desorption temperatures [8, 9, 10, 11]. These traits confine hydrides to stationary or niche applications rather than fast-fill vehicular refueling, where Type III/IV tanks remain dominant at 35–70 MPa.

From a grid-integration standpoint, hydrogen storage is most valuable for durations beyond batteries' economic range (multi-day to seasonal balancing), especially where

stored hydrogen also serves non-power uses, amortizing electrolyzer/compressor costs across revenue streams [5]. This is directly relevant to HRS design: compressors and cascade banks are increasingly viewed as potential demand-response nodes if charging is coupled to grid signals. This study’s finding – that charging *duration* (not terminal state) is freely controllable via compressor flow rate – suggests HRS recharging could be shifted to align with renewable surplus without altering the bank’s final pressure/temperature, provided safety limits are respected throughout.

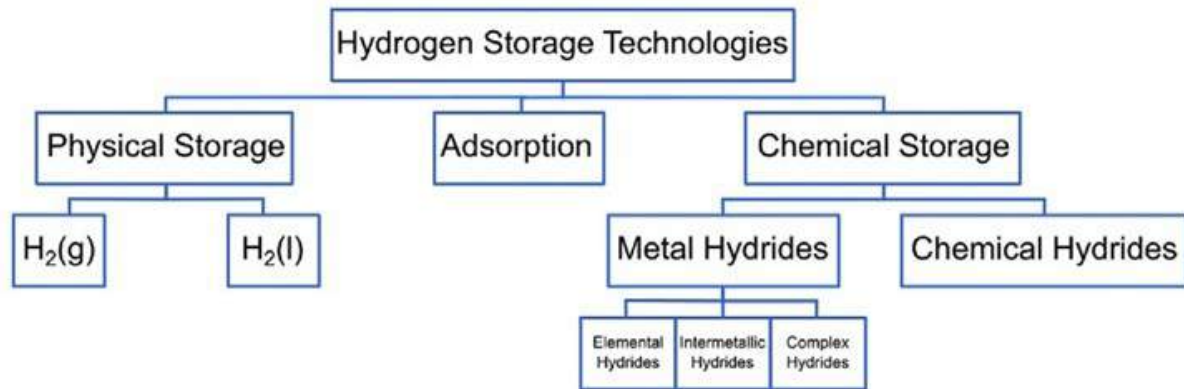


Figure 2: The applied categorization of hydrogen storage technologies

2.2. Hydrogen Refueling Station Architecture and Global Deployment

HRS deliver hydrogen at 35 MPa or 70 MPa via integrated subsystems: supply (delivery or on-site generation), multi-stage compression, cascade storage, pre-cooling, dispensing, and safety systems [12, 13]. Delivered hydrogen typically arrives at low pressure and is compressed to dispensing pressure; cascade storage minimizes compressor duty by drawing first from lower-pressure banks [14], organized in low/medium/high tiers (35–70 MPa). Pre-cooling to $\approx -40^\circ\text{C}$ mitigates compression and Joule–Thomson heating during fast fills per SAE J2601 [15]. Given hydrogen’s flammability and diffusivity, HRS incorporate relief devices, excess-flow valves, leak sensors, emergency shutdown, breakaway couplings, and facility mitigations (blast walls, open-air layouts), governed by ISO 19880 and SAE J2601 [15].

Previous system-level HRS investigations [14, 16] have modeled combined tank, compressor, heat-exchanger, and valve dynamics (via Dymola/Modelica) to analyze complete SAE J2601 refueling cycles. They illustrate that the number of cascade tiers and the pressure distribution dictate station energy use and compressor workload, with returns leveling off after roughly 3–4 tanks. However, because these analyses typically enforce fixed final station pressures, they fail to isolate how buffer-recharge behavior responds to varying compressor mass flow rates under a mass-based termination criterion—a gap addressed in the current work.

2.3. Hydrogen Storage Tank Classifications

Pressure vessels are classified into five types (I–V) by construction and load-bearing architecture (Table 1).

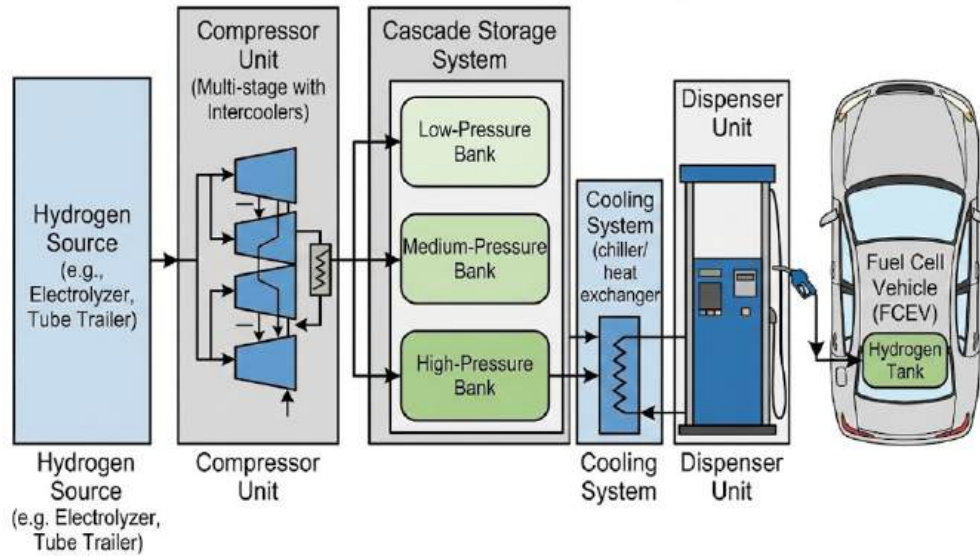


Figure 3: Schematic layout of a typical Hydrogen Refueling Station (HRS) with a Cascade Hydrogen Storage System (CHSS) [17]

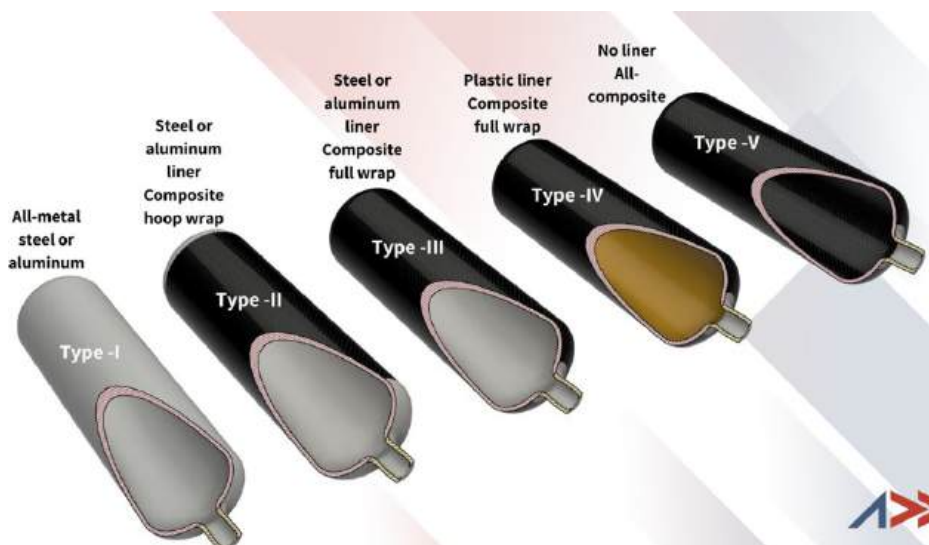
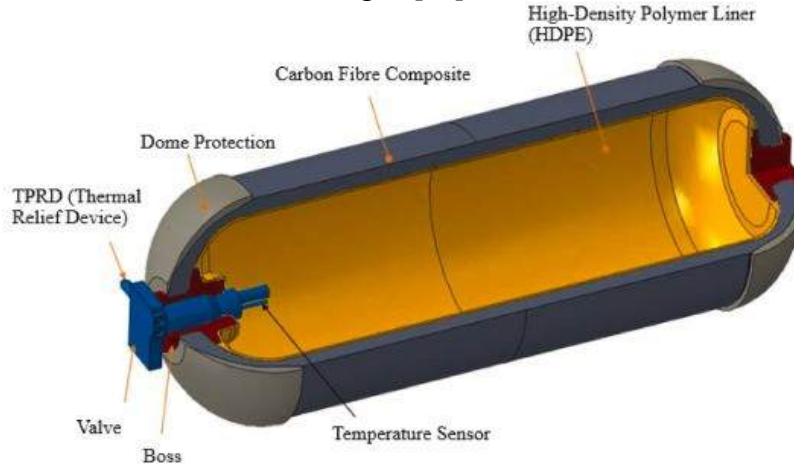


Figure 4: Types of Hydrogen Tanks [18]

- **Type I – All-metal. Steel/aluminum, ~20–30 MPa, low gravimetric efficiency (~1–2% H₂), embrittlement-prone; stationary, low-pressure use only [19].**
- **Type II – Metal liner, partial hoop wrap.** A thick metal liner with hoop-wound composite over the cylindrical section (unreinforced metal domes). Moderately lighter than Type I (~2–4% H₂ mass fraction), retaining the liner's impermeability and thermal mass. Rated to ~300–350 bar but commonly operated near 200 bar for buffer duty – the basis for this study's Type II blowdown scenario. Unreinforced

domes cap service pressure well below 700 bar, and the liner remains prone to embrittlement and interface fatigue [21].



- Figure 5: Components of type IV COPV [20]
- **Type III – Metal liner, full composite wrap.** A thin aluminum liner (e.g., 6061) fully wrapped in filament-wound carbon fiber carrying 90–95% of the load; the liner serves as an impermeability barrier. Enables up to 70 MPa with $\sim 4\times$ the gravimetric capacity of Type I, suiting high-pressure cascade banks (~ 450 – 500 bar) and early 35–70 MPa vehicle tanks [22]. Progressive-failure and composite-degradation studies identify fiber–matrix damage under cyclic pressure, liner fatigue, embrittlement, and thermal-stress delamination (from differential cooling rates during blowdown) as common degradation modes for Type III/IV vessels [23, 24].
- **Type IV – Polymer liner, full composite overwrap.** A non-metallic liner (HDPE/polyamide) fully encased in carbon-fiber/epoxy. Lightest configuration, 70 MPa working pressure (burst ~ 170 MPa), no metal embrittlement, and favorable leak-before-burst failure [23, 25]. Standard for 70 MPa onboard storage but outside this study’s 200–500 bar station-side scope.
- **Type V – All-composite (linerless).** Experimental, liner-free; potential weight/capacity gains limited by permeation and manufacturing complexity; not yet commercial [26].

Table 1: Comparison of hydrogen storage vessel classifications relevant to station infrastructure.

Type	Liner	Structural Load	Working Pressure	Typical HRS Role
I	Metal (steel/Al)	Metal wall only	~ 20 – 30 MPa	Low-pressure / stationary
II	Metal (steel/Al)	Hoop-wrapped composite	~ 20 – 35 MPa	Medium-pressure buffer (~ 200 bar)
III	Metal (Al, thin)	Full composite wrap	~ 50 – 70 MPa	High-pressure buffer (~ 500 bar)
IV	Polymer	Full composite wrap	~ 35 – 70 MPa	Onboard vehicle storage

	(HDPE)			
V	None	Composite only	Experimental	Research stage

Standards cap filling temperature at $\sim 85^{\circ}\text{C}$ and pressure overshoot at 125% of nominal, protecting the resin and liner. Type II/III vessels lack Type IV's intrinsic leak-before-burst behavior, since their metal liners crack rather than soften under extreme heat; they therefore rely on relief devices (burst disks, fusible plugs) and are qualified via cycling, drop, and bonfire testing per ISO 19881 and SAE J2579 [27, 28, 29].

2.4. *Alternative Storage Concepts: Cryogenic and Solid-State Approaches*

Cryo-compressed and cryogenic liquid storage offer higher volumetric density than room-temperature compressed gas. Aceves et al. show that cryogenic-capable vessels, operated across temperatures from cryogenic liquid to warm compressed gas, can match or exceed standard 70 MPa Type IV storage density with greater operational flexibility [30]. These approaches lie outside this study's 200–700 bar scope but represent a natural extension, since the CoolProp-based charging model used here could in principle extend to the two-phase/supercritical regions relevant to cryo-compressed storage.

Complex hydrides (alanates, borohydrides) offer higher gravimetric density than interstitial hydrides but require high desorption temperatures ($> 250^{\circ}\text{C}$ for Mg-based hydrides) and slower or partially reversible cycling, limiting deployment in fast-cycling HRS applications [10, 11, 31]; exothermic-absorption heat management further precludes 3–5 minute refueling. Zheng et al. situate compressed-gas vessels as the most mature technology for fast-cycling refueling relative to cryogenic and solid-state alternatives [32].

2.5. *Thermodynamics of High-Pressure Refueling and the Heat of Compression*

As storage pressures rose to 35–70 MPa, the central engineering challenge shifted from static capacity to transient thermal management. Early work attributed vehicle-tank heating during fast fills mainly to Joule–Thomson expansion; subsequent energy-balance analyses corrected this, showing that the work of compression – not Joule–Thomson heating – dominates (contributing $\sim 60\%$ of internal energy rise) [33, 34, 35, 36]. Models neglecting compression work underestimate final temperature and risk exceeding SAE J2601's 85°C limit [37, 38].

Striednig et al. use a real-gas formulation to show ideal-gas closure introduces significant error near 70 MPa [39], consistent with the real-gas (CoolProp) approach adopted here. Hosseini et al. similarly analyze coupled pressure–temperature–mass evolution during filling [40].

2.6. *Transient Evolution of Station-Side and Vehicle-Side System Parameters (P , T , m)*

Refueling involves time-dependent pressure, temperature, and mass interaction between station banks and vehicle tank. On the vehicle side, pressure rises linearly under the Average Pressure Ramp Rate (APRR) to prevent overheating. Rothuizen et al. characterize station-side pressure as a "sawtooth" profile [14]: as a bank discharges, pressure decays until the station–vehicle differential can no longer overcome the piping's loss coefficient (k_v), stalling flow and forcing a switch to a higher-pressure bank – the defining behavior of cascade efficiency, where poor switching logic risks premature compressor activation.

While the vehicle tank heats sharply, station vessels experience the opposite: expansion cooling (reverse Joule–Thomson effect), a significant, often-neglected source of inefficiency [41, 42]. Rapid discharge cools the vessel, reducing gas specific volume and collapsing tank pressure faster than mass depletion alone predicts – effectively reducing cascade usable capacity and forcing earlier bank switching.

Recharge aims to maximize stored hydrogen mass, a function of gas density at final cutoff pressure. High State of Charge (SOC) is thermodynamically limited by final temperature: without adequate heat-of-compression management via pre-cooling ($\approx -40^\circ\text{C}$), lower gas density under-fills the tank even at nominal target pressure [37] – a speed/SOC trade-off typically managed by throttling flow near the end of the fill.

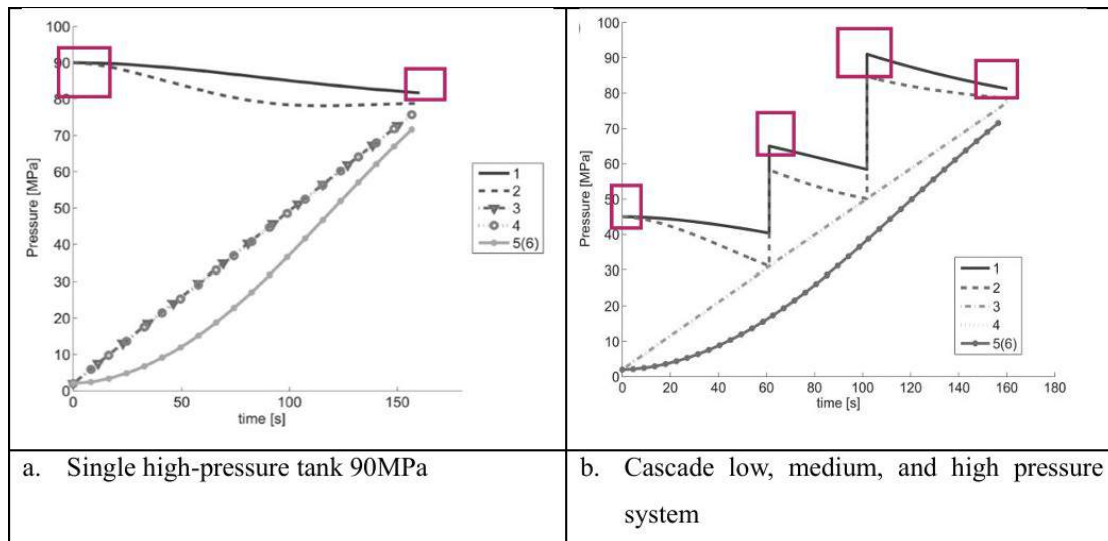


Figure 6: Pressure variation during onboard refueling: (a) single high-pressure storage tank at 90 MPa, decreasing to ~ 81 MPa; (b) cascade low-, medium-, and high-pressure system, with pressure varying across three stages ($45 \rightarrow 40$ MPa, $65 \rightarrow 58$ MPa, $90 \rightarrow 81$ MPa). [14]. Since final storage pressure hits a defined lower limit after each dispensing event (Fig. 6), station tanks must be recharged to restore pressure and mass inventory – the process examined by the charging model in Section 3.2.

2.7. Numerical Modeling Strategies and Research Gap

Given the cost of exhaustive physical testing, the field relies on simulation. Computational Fluid Dynamics (CFD) resolves localized thermal effects (e.g., buoyancy-driven stratification, jet-impingement heating) during fast fills [43] but is too costly for system-level parametric studies. Zero-dimensional (0-D) lumped-parameter models – assuming spatially uniform properties but retaining non-ideal gas behavior – are the validated tool for station-vehicle interface analysis, provided high-fidelity equations of state replace ideal-gas closure at high pressure [14, 39, 40].

Despite mature methods for isolated components (CFD tank safety, 0-D station energy models), an integrated framework coupling transient discharge cooling with subsequent recharging – evaluated jointly under varying final pressures, mass inventories, and flow rates – is largely absent; most studies assume constant supply conditions or fixed final pressure, overestimating performance and constraining design flexibility [14]. Similarly, the broader energy-storage literature (Section 2.1) addresses system/infrastructure-level metrics (capacity, efficiency, siting) rather than sub-cycle transient thermodynamics needed for safe compressor duty cycles and recovery-time estimation at the individual buffer-vessel level. This study addresses that gap via two

coupled dynamic models – adiabatic blowdown and adiabatic compressor charging – jointly capturing the full pressure–temperature–mass (P–T–m) trajectory of station buffer storage across the H35 and H70 tiers.

3. Methodology

The research methodology follows the sequential architecture depicted in the modeling workflow in Figure 7, advancing from physical system definition and thermodynamic governing balances to property closures, numerical solution schemes, and operational scenario definitions. Lumped-parameter models are developed: an ideal-gas adiabatic *blowdown* model characterizing rapid discharge of Type II and Type III buffer tanks, and a real-gas adiabatic *charging* model characterizing compressor recharging of H35 and H70 buffer tiers. Both models share the same conservation-law foundation but differ in equation-of-state fidelity, reflecting the different pressure regimes and the different sensitivity of each process to real-gas effects.

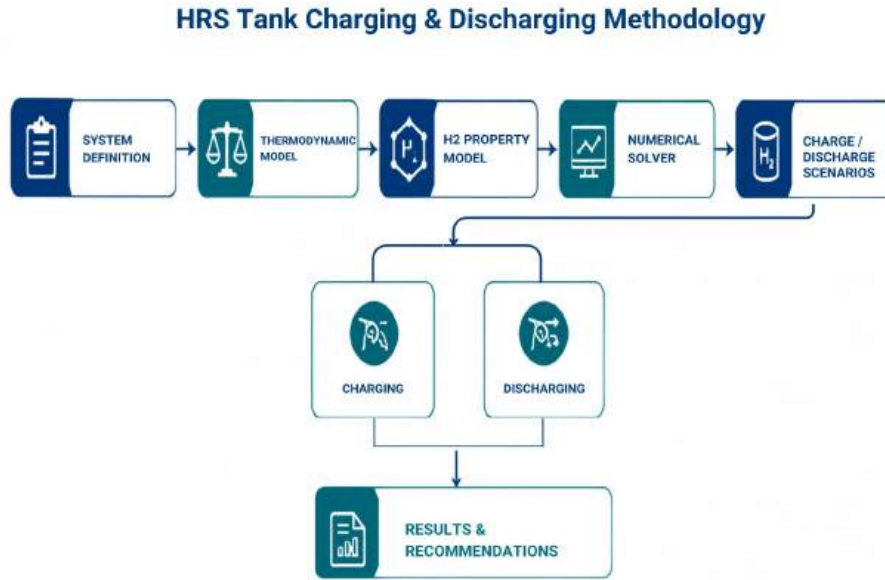


Figure 7: Methodology framework

3.1. Blowdown Model: Assumptions and Governing Equations

3.1.1. Model assumptions

Hydrogen is frequently stored in high-pressure tanks (35–70 MPa) for applications such as fuel cell vehicles. When a rapid depressurization event (blowdown) occurs, the gas expands adiabatically, resulting in a sharp drop in both internal pressure and temperature. All simulations assume a rigid tank (constant volume V) containing hydrogen modeled as an ideal gas, with the following

assumptions: the process is adiabatic ($\dot{Q} = 0$, no work exchange with the surroundings); the gas

state is spatially uniform (0-D); hydrogen obeys the ideal gas law; and the specific heats c_v , c_p (and hence $\gamma = c_p/c_v \approx 1.40$) are treated as constants evaluated at a representative temperature, with $R = 4124 \text{ J/(kg} \cdot \text{K)}$ for hydrogen. These simplifications retain the

essential thermodynamics of blowdown while keeping the problem numerically tractable.

3.1.2. Governing equations

Under these assumptions, mass and energy conservation for the control volume yield:

$$P(t) V = m(t) R T(t) \quad (1)$$

$$\frac{dm}{dt} = -\dot{m}_{out} \quad (2)$$

$$mc_v \frac{dT}{dt} + c_v T \frac{dm}{dt} = -\dot{m}_{out} c_p T \quad (3)$$

Hydrogen Tank (High Pressure)

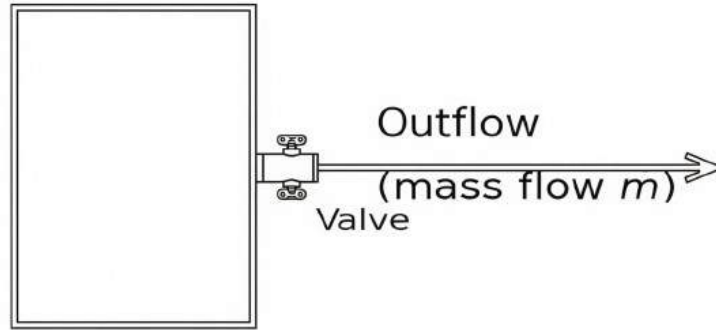


Figure 8: Schematic of the hydrogen tank discharge system. A high-pressure hydrogen tank is connected to an outlet valve through which gas escapes at mass flow rate $\dot{m}$. Adiabatic expansion leads to a reduction in both temperature and pressure of the remaining gas.

Substituting Eq. (2) into Eq. (3) and using $c_p/c_v = \gamma$ simplifies the temperature evolution to:

$$\frac{dT}{dt} = -(\gamma - 1) \frac{\dot{m}_{out}(t)}{m(t)} T(t) \quad (4)$$

Because $\gamma > 1$, any positive outflow drives $dT/dt < 0$, reflecting adiabatic expansion cooling of the residual gas. Instantaneous pressure follows directly from Eq. (1) once $m(t)$ and $T(t)$ are known:

$$P(t) = \frac{m(t) R T(t)}{V} \quad (5)$$

Equations (1)–(4) are integrated in MATLAB using the adaptive Dormand–Prince Runge–Kutta solver ode45, with an event function that halts integration when the tank pressure reaches atmospheric (≈ 1 bar), preventing unphysical negative mass or pressure. The initial state (m_0, T_0, P_0) is specified by first fixing P_0 and T_0 and computing $m_0 = P_0 V / (RT_0)$ from the ideal gas law.

3.1.3. Discharge scenarios

Three representative discharge scenarios are simulated (Table 2):

- **Scenario 1 – Constant outflow.** An idealized fixed-orifice discharge at $\dot{m} = 0.03$ kg/s from a Type II tank ($V = 3.0$ m³, $P_0 = 200$ bar, $T_0 = 300$ K, $m_0 \approx 48.5$ kg).
- **Scenario 2 – Decreasing (pressure-dependent) outflow.** A more realistic outflow that peaks near 0.04 kg/s and decays to zero by 300 s as the driving pressure differential falls, from the same 200 bar, 3.0 m³ initial state.
- **Scenario 3 – Increasing outflow, higher-pressure tank.** A Type III tank ($V = 3.0$ m³, $P_0 = 500$ bar, $T_0 = 300$ K, $m_0 \approx 121.2$ kg) vented through a linearly increasing outflow rate ($\approx 0.022 \rightarrow 0.028$ kg/s over 300 s), representing a controlled, progressively opening valve or increasing vent capacity; the tank does not empty within the simulated window.

Table 2: Blowdown model parameters and assumptions (ideal H₂, rigid tank, adiabatic, uniform state).

Scenario	V [m ³]	P_0 [bar]	T_0 [K]	Outflow law $\dot{m}(t)$	Time window
1 (Type II)	3.00	200	300	Constant, 0.03 kg/s	0–300 s
2 (Type II)	3.00	200	300	Pressure-dependent, decays to 0	0–300 s
3 (Type III)	3.00	500	300	Linear ramp, $\approx 0.022 \rightarrow 0.028$ kg/s	0–300 s

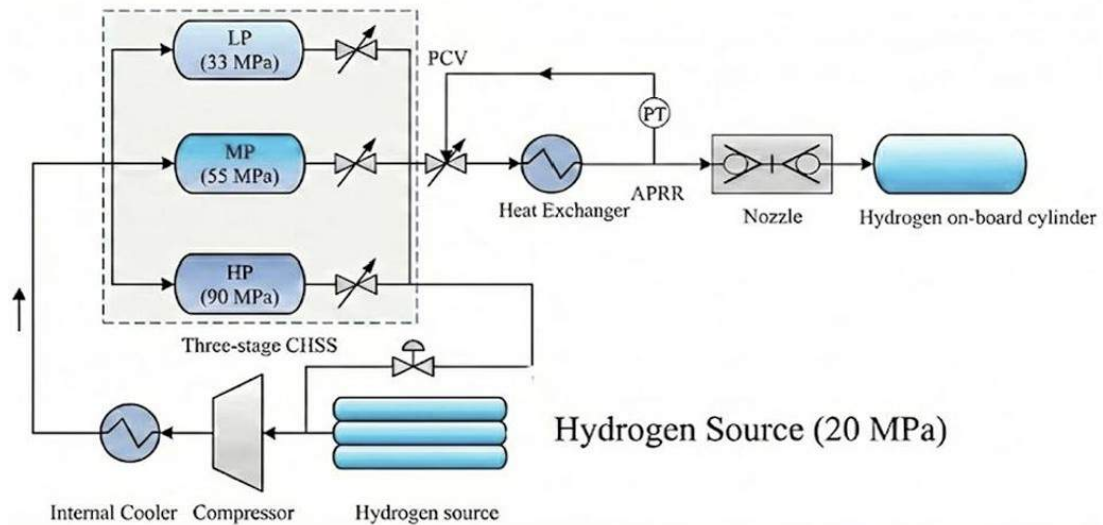


Figure 9: Simplified process diagram of the three-stage Cascade Hydrogen Storage System (CHSS) considered in the charging model, showing the low-pressure (33 MPa),

medium-pressure (55 MPa), and high-pressure (90 MPa) banks, the pressure-control valve (PCV) and average-pressure-ramp-rate (APRR) control at the dispenser, the heat exchanger, nozzle, and onboard cylinder, together with the compressor/intercooler recharging loop drawing from a 20 MPa hydrogen source.

3.2. Charging Model: Assumptions and Governing Equations

3.2.1. HRS operational context

The charging model represents the recovery phase of a CHSS following vehicle dispensing. In a representative three-stage cascade, (1) the low-pressure bank (~ 22 MPa) first charges the onboard tank from its initial pressure (e.g., 2 MPa) up to its own pressure level; (2) a second low-pressure bank (~ 33 MPa) continues charging until pressures equalize; (3) the medium-pressure (MP, ~ 55 MPa) and high-pressure (HP, ~ 90 MPa) banks then complete the fill to target mass and pressure; and (4) after dispensing, the LP, MP, and HP tanks must all be recharged to their original mass and pressure conditions using a multi-stage compressor with an intercooler, drawing from a low-pressure hydrogen source (e.g., ~ 20 MPa).

3.2.2. Governing equations

The charging analysis models an unsteady, adiabatic control volume ($\dot{Q} = 0$, $\dot{W} = 0$, $\dot{m}_{out} = 0$) into which hydrogen is introduced by a multi-stage compressor at enthalpy h_{in} (Fig. 10).

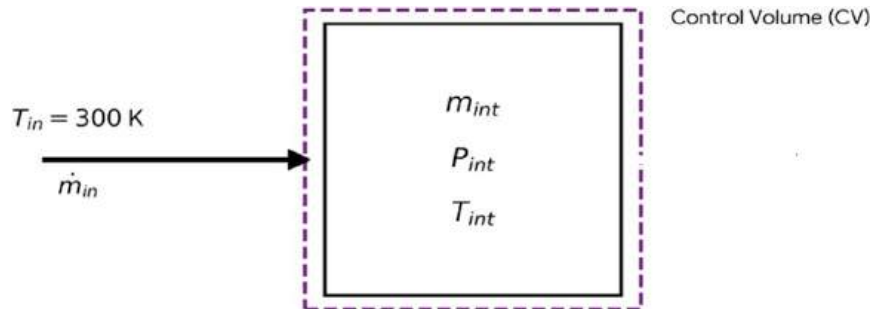


Figure 10: Control volume of the station storage tank during compressor charging. Hydrogen enters at $\dot{m}_{in}$ and T_{in} , raising the internal mass m_{cv} , pressure P_{cv} , and temperature T_{cv} of the control volume over time.

Mass and energy conservation give:

$$\frac{dm_{cv}}{dt} = \dot{m}_{in} \quad (6)$$

$$\frac{d(m_{cv}u_{cv})}{dt} = \dot{m}_{in}h_{in} \quad (7)$$

which reduces to an internal-energy evolution equation:

$$\frac{du_{cv}}{dt} = \frac{\dot{m}_{in}(h_{in}-u_{cv})}{m_{cv}} \quad (8)$$

Equation (8) highlights a fundamental property of adiabatic charging: because the internal-energy balance depends on the cumulative enthalpy delivered to the control volume rather than on the time history of the process, the *final* thermodynamic state (temperature and pressure) is independent of the compressor mass flow rate – variations in $\dot{m}_{in}$ affect only the *duration* of the charging event. This path-independence is a direct, testable consequence of the adiabatic assumption and forms a key theoretical expectation validated numerically in Section 4.2.

3.2.3. Real-gas property resolution via CoolProp

Because the charging analysis spans pressures approaching 100 MPa – well within the regime where hydrogen’s compressibility factor departs substantially from unity ($Z \approx 1.4$ near 70 MPa) – thermophysical properties are resolved at every integration step using the CoolProp library [44] rather than an ideal-gas closure. At each time step, the instantaneous density $\rho = m_{cv}/V$ and specific internal energy u_{cv} (from Eq. (8)) are used to query CoolProp for:

- Temperature: $T = f(u_{cv}, \rho)$;
- Pressure: $P = f(u_{cv}, \rho)$;
- Inlet enthalpy h_{in} , evaluated at the actual compressor delivery pressure and temperature rather than assumed constant.

The coupled system (Eqs. (6)–(8)) is integrated in MATLAB using ode45 (Dormand–Prince Runge–Kutta 4(5), adaptive time stepping), with CoolProp queried at every solver evaluation to update (T, P, h) – a tight coupling required to resolve the steep gradients that occur in the earliest stages of charging.

3.2.4. HRS parameters and SAE J2601 CHSS classification

Table 3 summarizes the overall station parameters adopted for context, including the SAE J2601 CHSS capacity category of the onboard tank relevant to the H35 and H70 tiers.

Table 3: Representative HRS parameters (station context for the charging model).

Parameter	Value
Tube-trailer (TT) pressure / volume	20 MPa / 5 m ³
Low-pressure (LP) bank / volume	33 MPa / 1 m ³
Medium-pressure (MP) bank / volume	55 MPa / 1 m ³
High-pressure (HP) bank / volume	90 MPa / 1 m ³
Chiller (pre-cooling) temperature	−40°C
Target dispensing pressure MPa (H35)	70 MPa (H70) / 35
Onboard tank size	Type B
Initial pressure in vehicle tank	2 MPa
Initial / ambient temperature	25°C

3.2.5. Charging simulation matrix

The charging simulations are terminated on a prescribed *target mass* rather than a target pressure, reflecting the operational logic of cascade HRS, where vessels are replenished according to inventory requirements. Because pressure and temperature are emergent state variables under this control policy, the model permits – and, as shown below, produces – pressure *overshoot* relative to nominal infrastructure ratings once the target mass is reached.

Table 4: Charging simulation parameters for the H35 (medium-pressure) and H70 (high-pressure) buffer tiers.

Tier	V [m ³]	m_0 [kg]	P_0 [MPa]	Target mass [kg]	$\dot{m}_{in}$ [kg/s]
H35	1.0	30–32 (step 1)	48.6, 50.7, 52.9	33.17	0.005, 0.01
H70	1.0	40–45 (step 1)	72.5–86.7	46.3	0.005, 0.01

The nominal (pre-overshoot) target pressures are 55 MPa for H35 and 90 MPa for H70. Higher initial mass inventories correspond to higher initial densities and internal energy content, and are expected to provide greater thermal inertia, reducing the temperature rise associated with a given increment of added mass – the “thermal buffering” effect examined quantitatively in Section 4.2.

4. Results and Discussion

4.1. Blowdown and Expansion Cooling Analysis

Scenario 1 (constant outflow, Type II, 200 bar). Under a constant 0.03 kg/s discharge, tank pressure falls almost linearly from 200 bar to approximately 122 bar over 300 s, while mass declines uniformly from ≈ 48.5 to ≈ 39.5 kg (a loss of ≈ 9.0 kg). The gas temperature drops from 300 K to 270–275 K over the same interval, a fall of 25–30 K driven by adiabatic expansion cooling as hydrogen leaves the tank. Because the outflow does not taper, the final increment of gas undergoes a comparatively abrupt expansion near $t \approx 300$ s, producing the sharpest instantaneous cooling rate of the scenario.

Scenario 2 (decreasing outflow, Type II, 200 bar). With outflow peaking near 0.04 kg/s and decaying to zero by 300 s, the pressure initially falls *faster* than in Scenario 1 (reflecting the higher initial $\dot{m}$), reaching approximately 80 bar by 300 s – lower than Scenario 1’s ≈ 120 bar – because more hydrogen is released early in the event. The corresponding temperature falls further,

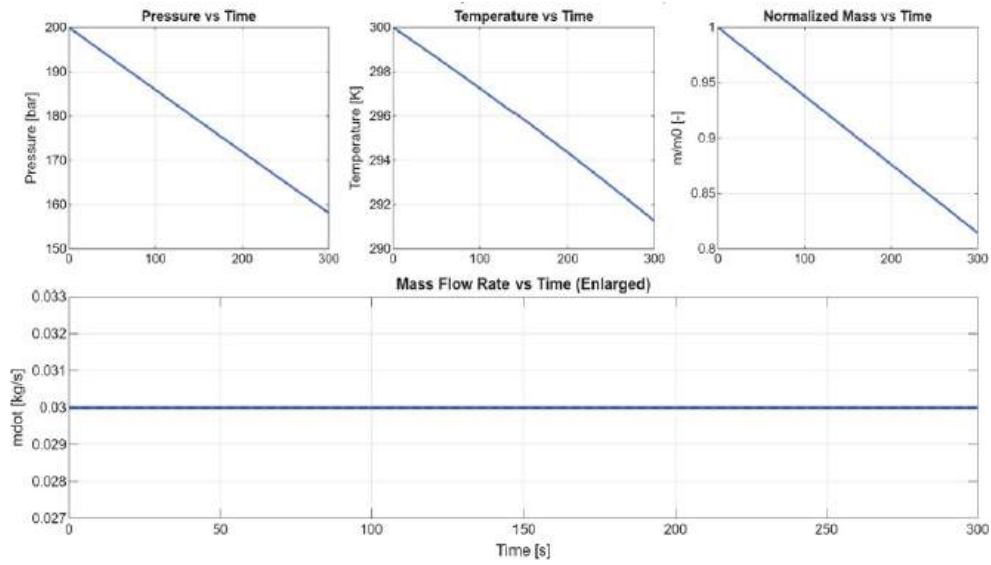


Figure 11: Scenario 1 simulation results (200 bar Type II tank, constant $\dot{m} = 0.03$ kg/s outflow): pressure, temperature, normalized mass, and mass flow rate vs. time.

into the 260–265 K range (and toward 200–230 K in the final seconds as the residual gas undergoes intense terminal expansion), reflecting the greater cumulative expansion. Unlike Scenario 1, the tapering outflow produces a smooth asymptotic approach to depletion rather than an abrupt end-of-discharge plunge, which is the physically preferable behavior for representing a real, pressure-throttled vent.

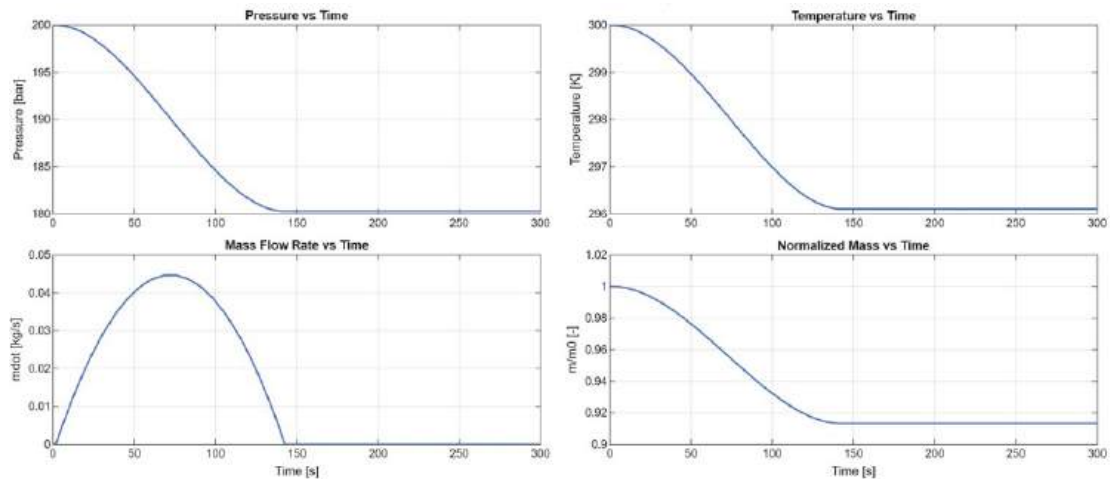


Figure 12: Scenario 2 simulation results (200 bar Type II tank, pressure-dependent decreasing outflow): pressure, temperature, mass flow rate, and normalized mass vs. time.

Scenario 3 (increasing outflow, Type III, 500 bar). With a much larger stored mass ($m_0 \approx 121.2$ kg) and a linearly ramping outflow ($\approx 0.022 \rightarrow 0.028$ kg/s), pressure falls only to

≈ 450 bar by 300 s (a drop of roughly 10% from the initial value) and temperature declines by only 10–12 K, to ≈ 288 –290 K. Only about 8–9 kg ($\approx 7\%$) of the initial mass is vented in the simulated window, versus 15–16 kg (≈ 31 –33%) in Scenario 2. Table 5 summarizes the three cases.

Effect of initial pressure at fixed volume and outflow. A supplementary comparison at

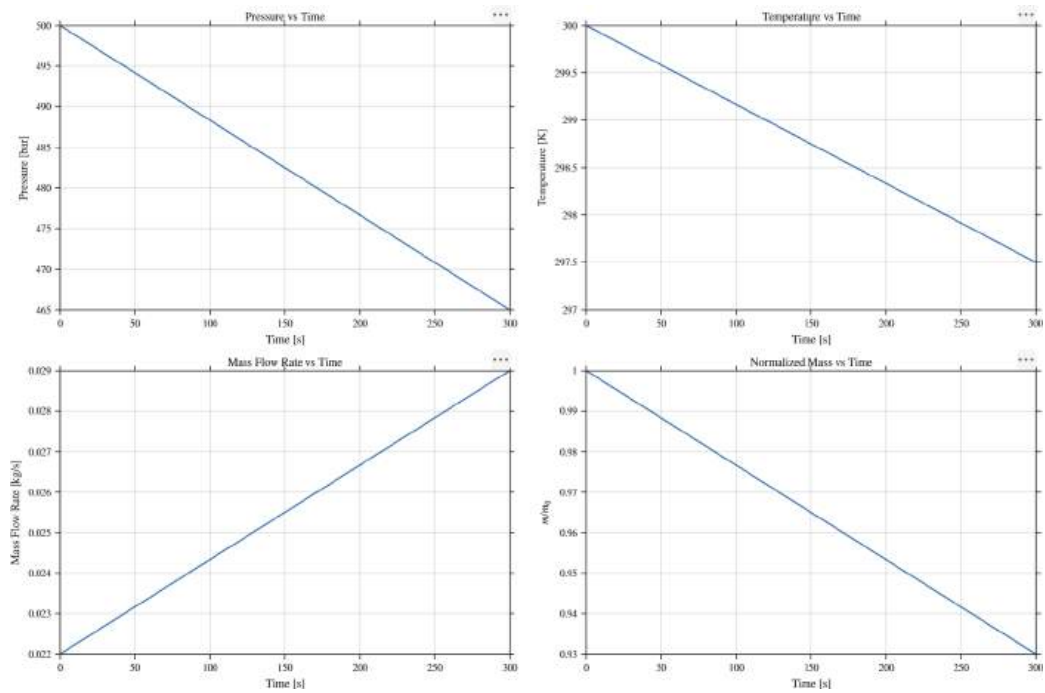


Figure 13: Scenario 3 simulation results (500 bar Type III tank, linearly increasing outflow): pressure, temperature, mass flow rate, and normalized mass vs. time.

Table 5: Comparison of blowdown scenarios: initial conditions and outcomes at $t = 300$ s.

Scenario	P_0 [bar]	$\dot{m}(t)$ profile	P_{300} [bar]	T_{300} [K]	m_0 [kg]	Vented [kg]
1 (Type II)	200	Constant, 0.03 kg/s	≈ 120	270–275	≈ 48.5	≈ 9.0
2 (Type II)	200	Pressure-dep. $\rightarrow 0$	≈ 80	260–265	≈ 48.5	≈ 15 –16
3 (Type III)	500	Linear 0.022 $\rightarrow$ 0.028	≈ 450	288–290	≈ 121	≈ 8 –9

fixed $V = 3.0 \text{ m}^3$ and constant $\dot{m} = 0.03 \text{ kg/s}$ across initial pressures of 200, 350, and 700 bar illustrates the buffering role of stored energy content. A 700 bar tank ($\approx 170 \text{ kg}$ initial mass) stores roughly twice the hydrogen of a 350 bar tank ($\approx 85 \text{ kg}$) and more than three times that of a 200 bar tank ($\approx 48.5 \text{ kg}$) at 300 K. Under identical venting, the 700 bar tank’s pressure barely moves (700 to ≈ 660 bar) with only slight cooling, the 200 bar tank drops to ≈ 163 bar and cools to $\approx 225 \text{ K}$, and the 350 bar case falls between the two. Proportional (percentage) mass and pressure losses are broadly similar across the three cases, but the *absolute* thermal and pressure excursions are far more pronounced at lower initial pressure – confirming that high-pressure tanks possess a substantially larger stored-energy buffer and change more slowly under identical flow conditions.

4.2. Compressor Charging and Thermal Buffering

4.2.1. H35 infrastructure (medium-pressure tier)

Under constant compressor flow, hydrogen mass in the H35 buffer accumulates linearly with time, and higher initial mass inventories reach the 33.17 kg target sooner.

At $t = 100$ s, mass reaches approximately 31/30.5, 32/31.5, and 33/32.5 kg (0.01/0.005 kg/s) for $m_0 = 30, 31$, and 32 kg, respectively. Quantitatively, charging duration falls from 317 s ($m_0 = 30 \text{ kg}$) to 118 s ($m_0 = 32 \text{ kg}$) at 0.01 kg/s, and from 634 s to 234 s at 0.005 kg/s – confirming that doubling

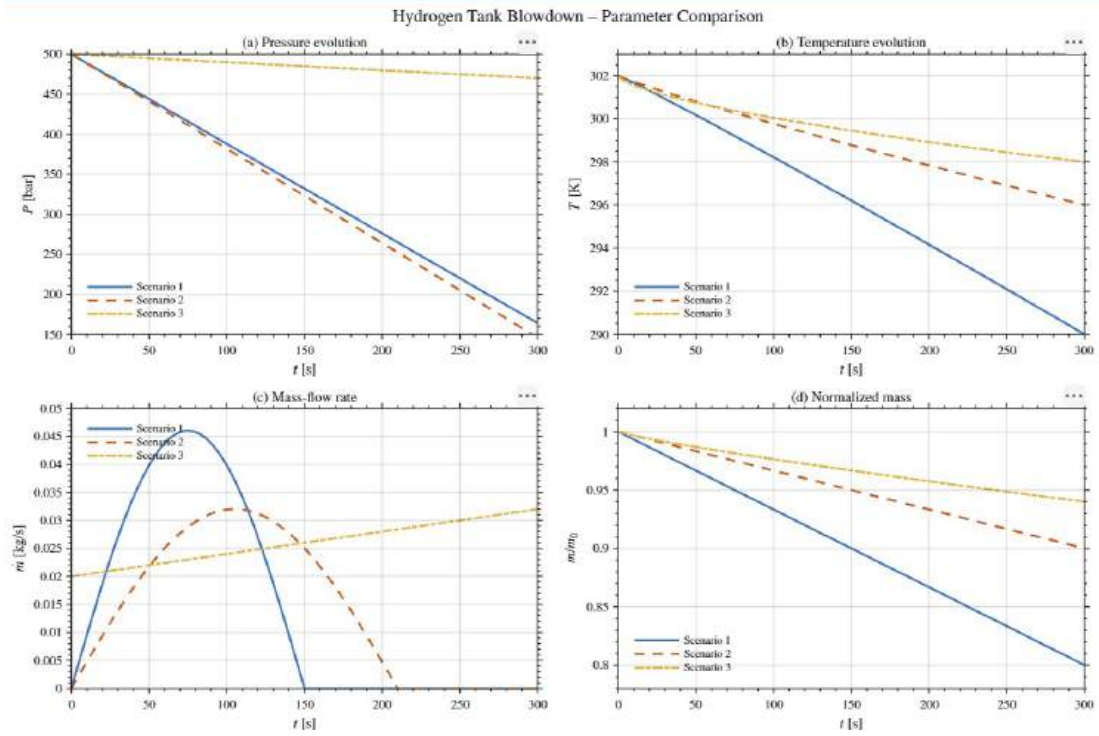


Figure 14: Overlaid comparison of pressure, temperature, mass flow rate, and normalized mass trajectories across the three blowdown scenarios.

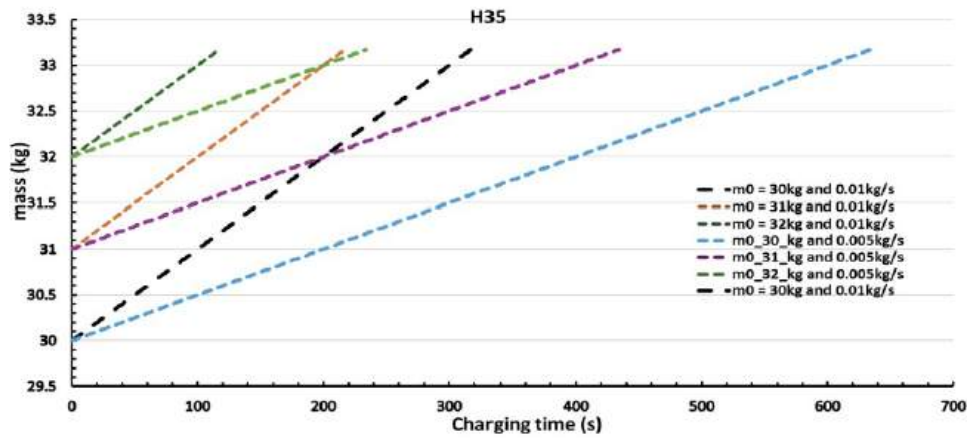


Figure 15: Temporal evolution of hydrogen mass during H35 charging for initial masses of 30, 31, and 32 kg at compressor flow rates of 0.01 and 0.005 kg/s. The compressor flow rate halves the charging time at every initial mass, independent of inventory level (Table 6). Gas temperature rises progressively with charging time; the influence of m_0 on the H35 temperature trajectory is comparatively small, while flow rate has a modest positive effect on the instantaneous temperature (at $t = 100$ s, ≈ 305 K at 0.01 kg/s versus ≈ 303 K at 0.005 kg/s), consistent with faster enthalpy delivery per unit time.

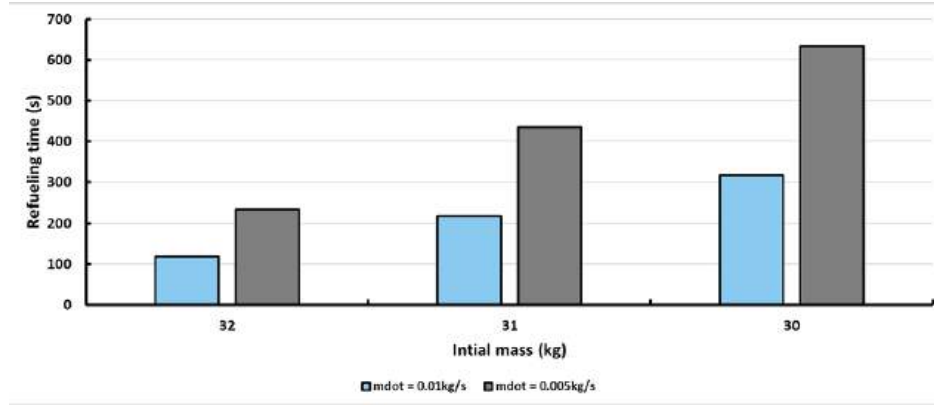


Figure 16: Total refueling duration for H35 storage configurations as a function of initial mass and compressor flow rate.

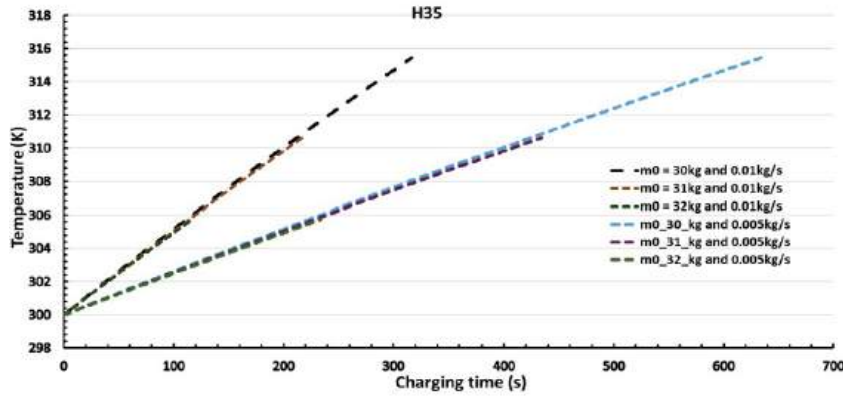


Figure 17: H35 gas temperature profiles as a function of charging time for different initial stored masses and compressor mass flow rates.

Pressure increases continuously with charging time; higher initial pressures reach the target sooner, and the final pressures – because the model is mass-terminated – overshoot the nominal 55 MPa target, reaching 58.5, 57.7, and 56.7 MPa for initial pressures of 48.6, 50.7, and 52.9 MPa, respectively. Flow rate has no significant effect on this terminal pressure, confirming the path-independence predicted by Eq. (8).

Table 6: H35 charging duration and terminal states as a function of initial mass and compressor flow rate.

m_0 [kg]	Δt (0.01 kg/s) [s]	Δt (0.005 kg/s) [s]	P_{term} [MPa]
30 (48.6)	317	634	58.5
31 (50.7)	217	434	57.7
32 (52.9)	118	234	56.7

4.2.2. H70 infrastructure (high-pressure tier)

At 0.01 kg/s, the H70 target mass of ≈ 46.3 kg is reached in 630, 530, 430, 330, 230, and 130 s for initial masses of 40 through 45 kg, respectively; at 0.005 kg/s the corresponding durations approximately double, to 1256, 1056, 856, 656, 456, and 256 s. Mass accumulates linearly with time.

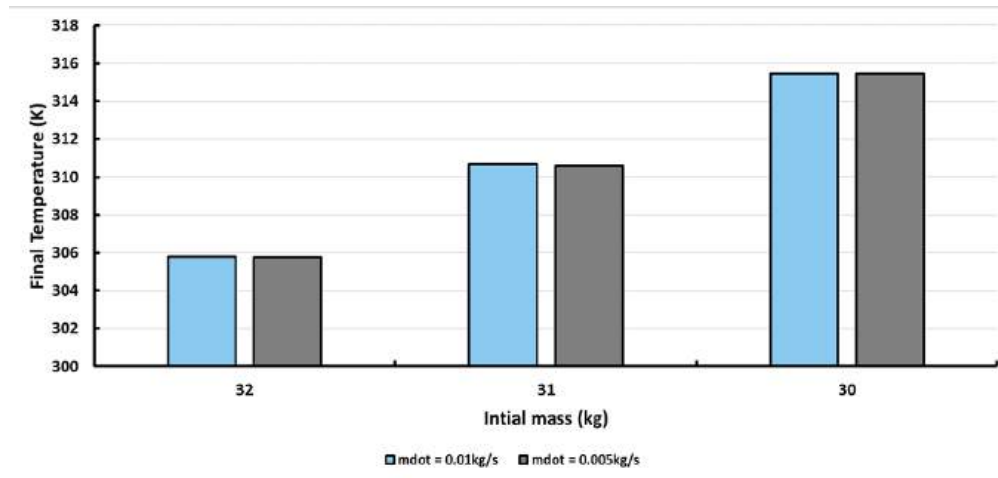


Figure 18: Final gas temperatures for H35 system states as a function of initial mass and compressor flow rate.

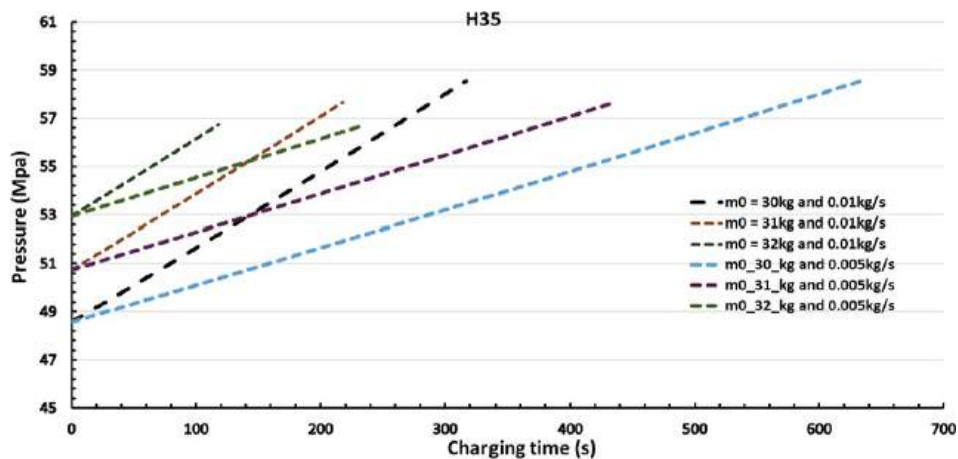


Figure 19: Pressure development during H35 infrastructure charging as a function of time, initial pressure, and compressor flow rate.

in every case: at $t = 100$ s, mass reaches approximately 41, 42, 43, 44, 45, and 46 kg for initial masses of 40 through 45 kg (0.01 kg/s).

Gas temperature increases steadily with charging time at a fixed flow rate. At $t = 100$ s (0.01 kg/s), the temperature reaches 304.25, 304.18, 304.13, 304.07, 304.01, and 303.96 K for $m_0 = 40$ through 45 kg, respectively, a small spread reflecting the near-instantaneous dominance of enthalpy input over residual initial-state differences.

However, the terminal temperature, reached once the target mass is achieved, shows a pronounced dependence on initial mass, since lower initial inventories require the addition of proportionally more high-enthalpy gas: peak (terminal) temperatures reach approximately 324.4, 320.6, 316.7, 312.9, 308.9, and 305.1 K for $m_0 = 40$ through 45 kg, respectively (Table 7). This constitutes the study's clearest demonstration of thermal buffering: increasing m_0 from 40 to 45 kg lowers the terminal temperature by

approximately 20 K, and compressor flow rate has no significant effect on this terminal value. Pressure evolves analogously: at $t = 100$ s (0.01 kg/s), the pressure reaches approximately 76.3,

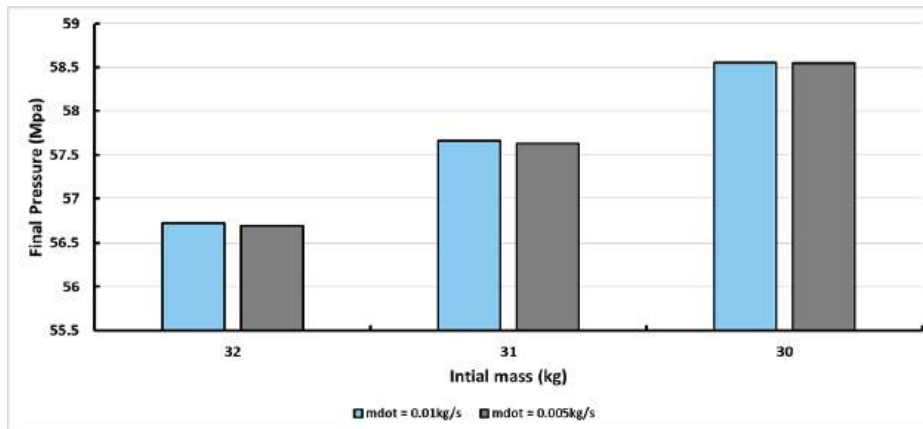


Figure 20: Final pressure distribution for H35 charging scenarios, showing overshoot relative to the nominal 55 MPa target.

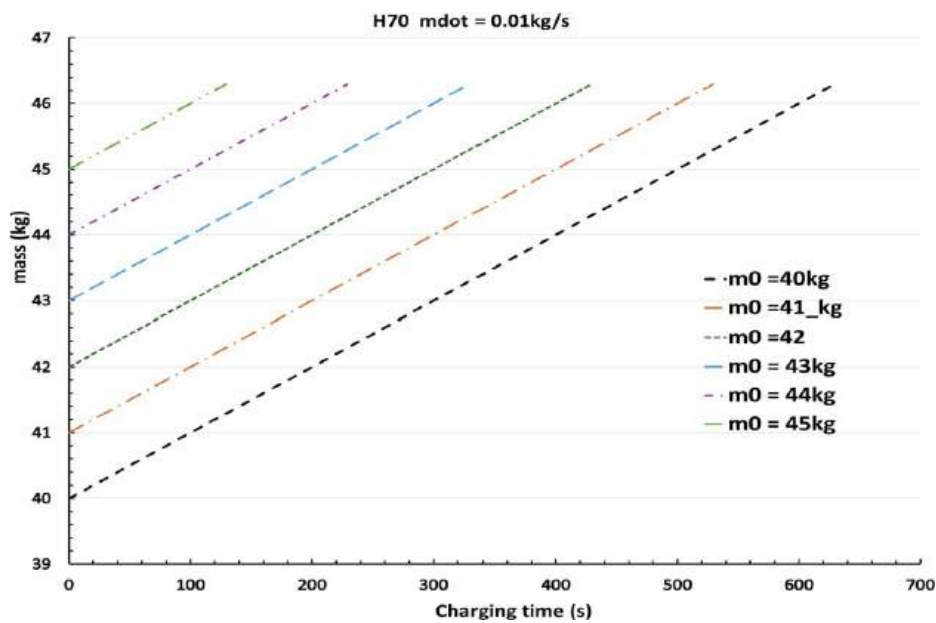


Figure 21: H70 mass accumulation profiles at 0.01 kg/s compressor flow rate for initial masses of 40–45 kg.

79.1, 81.9, 84.9, 87.8, and 90.9 MPa for initial pressures ranging from 72.5 through 86.7 MPa. Because charging is mass-terminated against a nominal 90 MPa target, final pressures again overshoot, reaching 98.0, 96.8, 95.7, 94.5, 93.3, and 92.1 MPa for $m_0 = 40$ through 45 kg, with the overshoot being largest for the lowest initial mass inventory.

Compared with H35 at the same flow rate, H70 charging duration is nearly double, owing to its larger stored-mass increment and higher operating pressure, consistent with a proportionally greater cumulative enthalpy requirement. Across every simulated H35 and H70 case, the maximum gas temperature (324.4 K, or 51.3°C) remains well below

the 358.15 K (85°C) safety threshold mandated for composite pressure vessels, with a margin of approximately 33.7 K under the most thermally demanding condition (H70, $m_0 = 40$ kg).

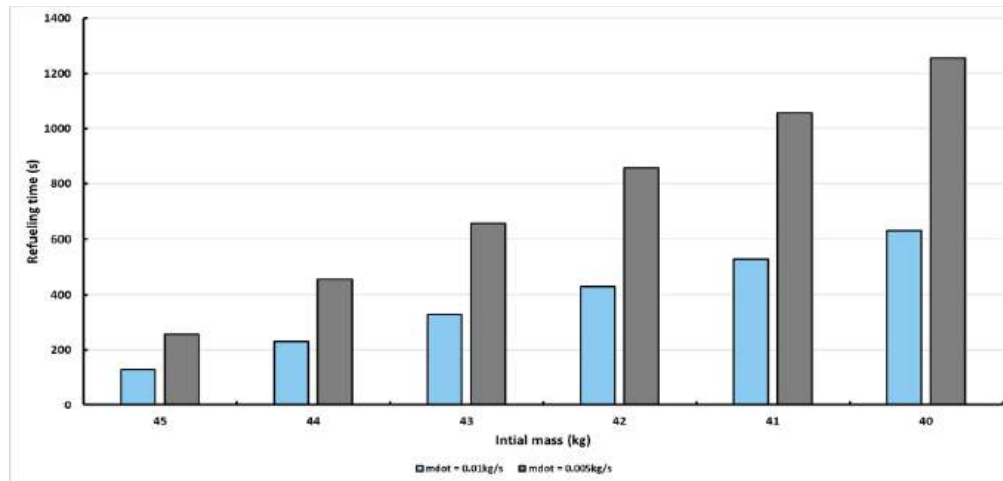


Figure 22: Comparative refueling times for H70 infrastructure tiers across initial mass inventories and compressor flow rates.

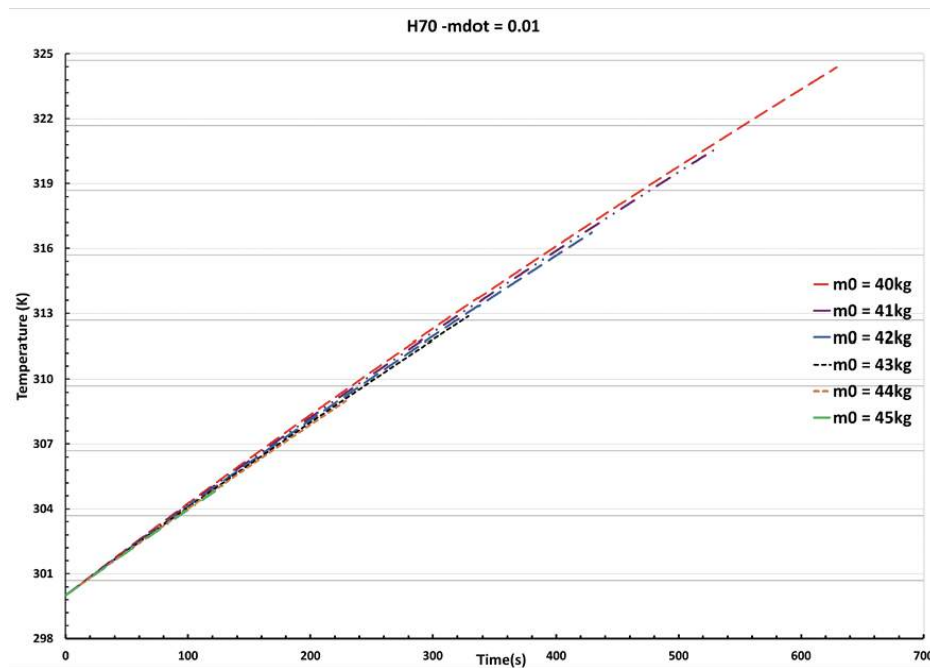


Figure 23: High-pressure thermal evolution for H70 charging operations: gas temperature vs. time for initial masses of 40–45 kg at 0.01 kg/s.

Table 7: H70 terminal states and refueling duration as a function of initial mass inventory.

m_0 [kg]	Dur. @ 0.01 kg/s [s]	Dur. @ 0.005 kg/s [s]	T_{term} [K]	P_{term} [MPa]
40	630	1256	324.4	98.0
41	530	1056	320.6	96.8

42	430	856	316.7	95.7
43	330	656	312.9	94.5
44	230	456	308.9	93.3
45	130	256	305.1	92.1

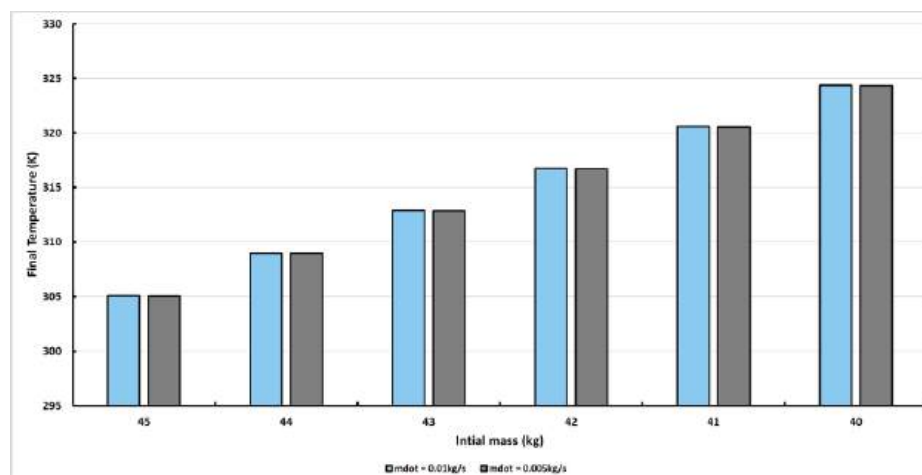


Figure 24: Final temperature results for H70 charging configurations, illustrating the thermal-buffering effect of higher initial mass inventory.

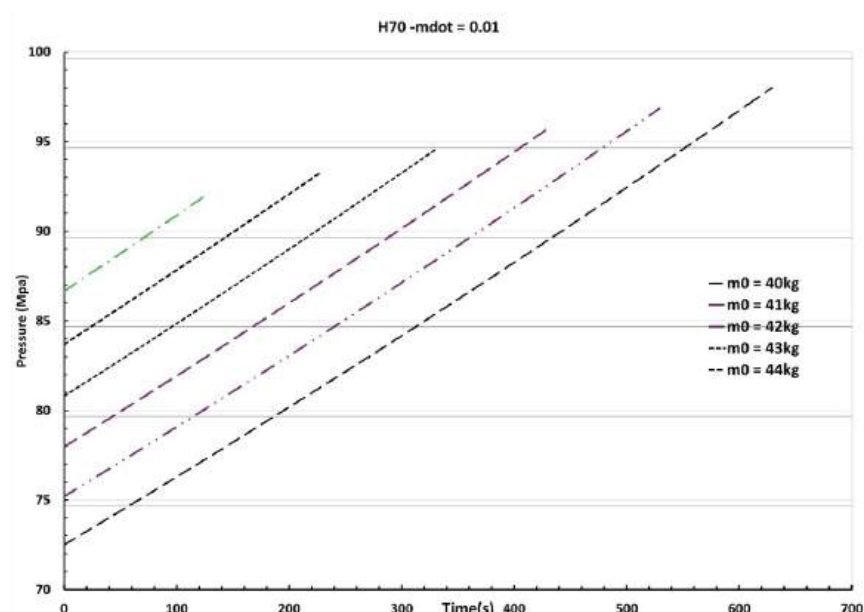


Figure 25: Pressure trajectory for H70 high-pressure infrastructure charging at 0.01 kg/s for initial pressures of 72.5–86.7 MPa.

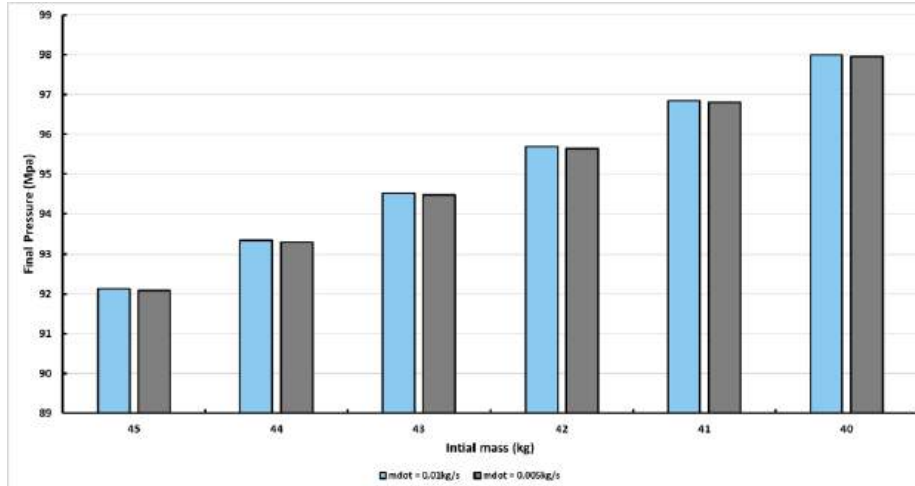


Figure 26: Final pressure summary for H70 charging cycles, showing overshoot relative to the nominal 90 MPa target.

4.3. Synthesis: Discharge and Charge as a Coupled Duty Cycle

Read together, the blowdown and charging analyses characterize opposite phases of the same operational cycle experienced by a station buffer vessel. During discharge, expansion cooling can drive gas temperature down by up to ~ 30 K in a lower-pressure (Type II, 200 bar) tank within minutes, while a higher-pressure (Type III, 500 bar) tank of equal volume cools by only a third as much under comparable venting, owing to its substantially larger thermal and mass reservoir. During the subsequent recharge, the same buffering logic reappears in reverse: higher initial mass inventories (i.e., *shallower* depletion during the preceding discharge) reduce the peak heating experienced during recharge by tens of kelvin. Both processes are therefore governed by the same underlying principle – specific internal energy change per unit mass transferred is inversely related to the thermal inertia of the initial inventory – and both point toward the same operational conclusion: minimizing the depth of discharge of high-pressure buffer banks simultaneously limits blowdown cooling severity (relevant to material embrittlement and valve icing risk) and recharge heating severity (relevant to the 85°C composite safety threshold). In addition, because the charging terminal state is a function of cumulative enthalpy addition rather than compressor flow rate (Section 4.2), station operators retain a free control variable – flow rate – to manage recharge *duration* for demand-response purposes without affecting the final thermodynamic state, whereas the blowdown analysis shows that the appropriate control variable for managing discharge behavior is instead the venting/outflow profile itself, since it directly determines both the terminal pressure and terminal temperature reached before the tank is switched or refilled.

5. Conclusion

This study developed and jointly presented two zero-dimensional thermodynamic models describing the complete duty cycle of hydrogen refueling station buffer storage: rapid adiabatic blowdown and subsequent compressor recharging. The principal findings are:

1. Blowdown severity scales inversely with stored-energy buffer. Under constant discharge, a 200 bar (Type II) tank cools by 25–30 K within 300 s, whereas a 500 bar (Type III) tank of equal volume cools by only 10–12 K, because its larger mass and internal-energy inventory buffers the expansion. Both tank size and initial pressure critically govern the severity of expansion cooling.

2. Outflow profile shape governs the manner, not just the magnitude, of depressurization. A constant outflow produces a comparatively abrupt terminal expansion and the coldest instantaneous gas temperatures near depletion, while a pressure-dependent (decaying) outflow yields a smoother, more physically realistic approach to depletion – an important consideration for both safety-system design and model fidelity.
3. Charging duration scales inversely with compressor mass flow rate, while the terminal thermodynamic state does not. Doubling the compressor flow rate from 0.005 to 0.01 kg/s halves charging duration in both H35 and H70 tiers without altering final pressure or temperature – a direct, numerically confirmed consequence of the adiabatic energy balance depending on cumulative enthalpy input rather than the rate of its delivery.
4. Initial mass inventory provides substantial thermal buffering during recharge. In the H70 tier, raising m_0 from 40 to 45 kg lowers the peak (terminal) gas temperature by approximately 20 K (324.4 K to 305.1 K), and analogous effects on terminal pressure overshoot are observed in both tiers.
5. All simulated charging scenarios comply with the 358.15 K (85°C) safety threshold, with a minimum margin of ≈ 33.7 K under the most demanding H70 case, but mass-based termination criteria alone permit pressure overshoot beyond nominal ratings (up to 58.5 MPa for H35 against a 55 MPa target, and 98.0 MPa for H70 against a 90 MPa target), indicating that mass-based control strategies must be coupled with explicit pressure ceilings.

5.1. Recommendations for Station Operation

Based on the combined discharge/charge analysis, the following operational strategies are recommended:

1. Dual-constraint control logic. Replenishment algorithms should not rely on mass targets alone; explicit pressure ceilings should be enforced in parallel to prevent over-pressurization arising from hydrogen’s non-ideal compressibility at high pressure.
2. Shallow cycling of high-pressure banks. High-pressure (H70-tier and Type III) banks should avoid deep depletion where operationally feasible. Maintaining a higher “heel” pressure/mass simultaneously reduces blowdown cooling severity and provides thermal buffering during the subsequent recharge, lowering thermal and mechanical stress on the vessel liner across the full cycle.
3. Realistic outflow modeling. Station-level safety and performance models should employ pressure-dependent (rather than constant) outflow laws for blowdown analysis, since constant-outflow assumptions overstate terminal cooling severity and produce non-physical abrupt depletion behavior.
4. Protocol integration. The adiabatic 0-D models presented here are well suited to rapid operational screening and recovery-time estimation, but should be used in conjunction with established fueling protocols (e.g., SAE J2601) to ensure compliance with dynamic pressure ramp-rate requirements not explicitly modeled here.

5.2. Limitations and Future Work

Both models involve simplifications that bound their quantitative accuracy. The blowdown model assumes ideal-gas behavior with constant specific heats and neglects

heat transfer with the environment; at the high pressures and low temperatures reached in the more extreme scenarios, real-gas and non-adiabatic effects would moderate the predicted cooling, and the model's very low terminal temperatures in the final seconds of discharge should be interpreted as an idealized worst case rather than a literal prediction (phase change is also not modeled, which would become relevant below hydrogen's liquefaction/solidification range). The prescribed outflow laws for Scenarios 2 and 3 are imposed rather than derived from orifice/choked-flow physics; coupling $\dot{m}_{\text{out}}$ to the internal pressure via compressible-flow relations would remove this dependency and automatically capture the transition from choked to subsonic venting as pressure falls.

The charging model, while incorporating real-gas effects via CoolProp, remains adiabatic and 0-D: it does not resolve gas–wall heat transfer (which would likely further increase safety margins by dissipating some compression heat to the vessel structure and surroundings), nor spatial gradients or stratification within the tank that only a CFD approach could resolve, nor the pressure losses and heat of compression generated within the compressor and piping assembly upstream of the control volume.

Future work should therefore: (i) integrate non-adiabatic gas–wall heat transfer correlations (Nusselt-number-based) into both models; (ii) couple discharge outflow to internal pressure via choked/subsonic orifice relations; (iii) extend the charging control volume to a system-level “grid-to-nozzle” analysis including compressor and piping losses; and (iv) validate both 0-D models against CFD or experimental data to quantify the magnitude of the spatial-averaging and adiabatic-assumption errors identified above.

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None

Conflict of Interest

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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