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# New-Generation Refrigerants: Performance Analysis, AI-Driven Prediction, Thermodynamic Modelling, And Environmental Transition

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***Abstract- The accelerating phase-down of hydrofluorocarbons (HFCs) under the Kigali Amendment to the Montreal Protocol has intensified global research into low-global-warming-potential (GWP) refrigerants that can meet the dual imperatives of environmental sustainability and thermodynamic efficiency. This paper presents a comprehensive review of emerging refrigerant classes — including hydrofluoroolefins (HFOs), hydrochlorofluoroolefins (HCFOs), natural refrigerants ($CO_2$, ammonia, hydrocarbons), and novel blends — evaluating their thermophysical properties, cycle performance, safety classifications, and compatibility with existing vapor-compression infrastructure. A comparative thermodynamic analysis is conducted using the coefficient of performance (COP), volumetric refrigerating capacity, and exergy efficiency as primary benchmarks. Special attention is given to HFO- 1234yf, HFO-1234ze(E), and R-290 (propane) as front-runner replacements in residential, commercial, and automotive refrigeration sectors. The study further examines regulatory frameworks, material compatibility challenges, lubricant interactions, and the economic feasibility of retrofit and drop-in solutions. Findings indicate that while no single refrigerant universally replicates the performance of incumbent HFCs, optimized low-GWP blends and $CO_2$-based trans critical systems demonstrate strong potential across a broad range of applications. This work aims to inform engineers, policymakers, and manufacturers in navigating the ongoing refrigerant transition toward a climate-responsible cooling industry.***

***Index Terms- Refrigerant Science, Thermal Engineering, Environmental Impact, HFO Blends, AI/Data Mining, Vaporisation Theory, R-410A Alternatives, Regulatory Compliance***

## I. INTRODUCTION

Refrigeration and air conditioning represent foundational pillars of modern civilization, underpinning food safety, thermal comfort, pharmaceutical storage, and industrial process control. The working fluids at the heart of these systems — refrigerants — have undergone successive generational transitions driven by evolving understanding of their environmental consequences. From the flammable and toxic first-generation natural refrigerants, through the ozone-depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), to the climate-active hydrofluorocarbons (HFCs), each transition has been prompted by a new class of environmental concern.

The current generation of HFC refrigerants — including R404A, R410A, R134a, and R22 — faces mandatory phase-down under the 2016 Kigali Amendment to the Montreal Protocol and regional regulations such as the European Union F-Gas Regulation (EU 517/2014). These fluids carry global warming potential (GWP) values ranging from hundreds to nearly four thousand times that of CO2 on a 100-year horizon. The task before refrigeration engineers is to identify fourth-generation replacements— principally Hydrofluoroolefins (HFOs) and their blends — that retain the safety, efficiency, and practical characteristics of HFCs while dramatically reducing environmental impact.

This review examines four carefully selected studies that illuminate different dimensions of this challenge. The first provides a broad scientific framework from NIST researchers; the second addresses the physical characterization and safety validation of a novel HFO mixture targeting R-410A replacement; the third introduces artificial intelligence as a rapid performance prediction tool for new HFO blends; and the fourth applies a rigorous statistical mechanics framework to derive the thermodynamic properties of refrigerants from first principles. Together, they demonstrate that navigating the transition to sustainable refrigerants demands simultaneous advances in chemistry, safety engineering, computational intelligence, and fundamental thermodynamic theory.

## II. BACKGROUND AND REGULATORY CONTEXT

### 2.1 The Refrigerant Generational Framework

The history of refrigerants can be organized into four generations, as articulated by Calm (2008) and elaborated by McLinden et al. (2020). The first generation comprised natural refrigerants — ammonia, CO2, sulfur dioxide, hydrocarbons — used primarily in industrial settings before the 1930s. The second generation, dominated by CFCs and HCFCs (known commercially as 'Freons'), prioritized safety and stability, enabling the explosive growth of domestic and commercial refrigeration. These were phased out under the 1987 Montreal Protocol after being definitively linked to stratospheric ozone depletion.

Third-generation HFCs addressed the ozone depletion problem but introduced a new concern: high GWP arising from their long atmospheric lifetimes and heat-trapping properties. The Kyoto Protocol (1997) listed HFCs as greenhouse gases. The 2016 Kigali Amendment mandates an 85% reduction in GWP-weighted HFC production by 2036 for developed countries. Fourth-generation refrigerants — principally the HFOs (hydrofluoroolefins), often blended with HFC components — are characterized by the carbon- carbon double bond that dramatically reduces atmospheric lifetime (days to weeks versus years for HFCs), yielding GWP100 values typically below 10.

### 2.2 Regulatory Drivers

Several regulatory frameworks are actively driving the transition. The EU F-Gas Regulation (517/2014) introduces a quota-based phase-down of HFCs and prohibits the use of refrigerants with GWP > 150 inmany new installations. The US EPA Significant New Alternatives Policy (SNAP) program has listed several HFCs as unacceptable in key applications. Japan's revised Fluorocarbons Act implements similar restrictions. The practical consequence is that refrigerants such as R404A (GWP 3,943), R410A (GWP 2,090), and R134a (GWP 1,300) are being phased out of new equipment across major markets, creating urgent demand for validated, commercially deployable alternatives

### 2.3Constraints on Refrigerant Selection

As McLinden et al. comprehensively outline, no perfect refrigerant exists. The desired properties span thermodynamic (vapor pressure, density, heat capacity matched to the application), safety (low toxicity, minimal flammability), environmental (zero ODP, low GWP), chemical (stability, materials compatibility), and practical (reasonable cost, long availability) dimensions. The tension between low flammability and low GWP is particularly challenging: higher fluorine substitution suppresses flammability but also tends to increase GWP. Most low-GWP HFO candidates carry an A2L classification (mildly flammable), requiring revised safety codes and system designs.

## III. STUDY 1 — NEW REFRIGERANTS AND SYSTEM CONFIGURATIONS FOR VAPOR- COMPRESSION REFRIGERATION

McLinden, Seeton, and Pearson (Science, 2020) — representing researchers from NIST, Shrieve Chemical Products, and Star Refrigeration — provide the most comprehensive recent overview of the refrigerant transition landscape, published in the prestigious journal Science.

### 3.1Thermodynamic Requirements

The authors systematically establish the thermodynamic parameters that govern refrigerant selection. The key variables are the liquid-vapor critical temperature and pressure together with the vapor heat capacity, which together determine the operating pressures, volumetric capacity, and energy efficiency of the refrigeration cycle. The search space is inherently limited: volatile fluids suitable as refrigerants must be small molecules (one to four carbons) with boiling points typically from -50°C to +30°C. A comprehensive systematic search identified that most low-GWP options are at least slightly flammable an unavoidable consequence of the molecular modifications that reduce both GWP and flammability being in direct tension.

### 3.2The HFO Landscape

Among the HFOs, propene-based compounds (three-carbon) with four to six fluorine substitutions are the primary candidates. HFO-1234yf (2,3,3,3-tetrafluoropropene, A2L, GWP < 1) has achieved dominant status in automotive air-conditioning, now used in the majority of new vehicles in the EU, US, and Japan. HFO-1234ze(E) (trans-1,3,3,3-tetrafluoropropene, A2L, GWP < 1) has been commercialized as a foam- blowing agent and refrigerant in chillers. The four-carbon HFO-1336mzz(Z) offers a non-flammable, low- pressure option for chiller applications, while the related HCFOs (containing chlorine with minimal ODP < 0.001) such as HCFO-1233zd(E) are also finding niche applications.

For R-410A replacement in small air-conditioning systems, no single-component non-flammable HFO with comparable thermodynamic properties exists. The study surveys numerous blends containing combinations of HFO-1234yf, HFO-1234ze(E), HFC-134a, and HFC-125 that have been proposed. Non-flammable blends require high concentrations of HFC-125 or HFC-134a, resulting in GWP100 values from 540 to over 2,000 — acceptable as interim solutions but insufficient for long-term Kigali compliance. Blends with 2L flammability classification and GWP100 of 100 to 500 represent a more sustainable medium-term solution.

### 3.3Natural Refrigerants: Resurgence

The authors note a significant resurgence of interest in the classical natural refrigerants — ammonia (NH3), carbon dioxide (CO2), propane (C3H8), and isobutane (iC4H10). All have zero ODP and near-zero GWP. By 2020, hydrocarbons accounted for 75% of global household refrigerator production, a transformation sparked by the 'Greenfreeze' initiative. CO2 is being widely deployed in supermarkets, ice rinks, heat pump water heaters, and automotive systems, though achieving high efficiency with CO2 requires more complex system configurations than conventional fluorocarbons. Ammonia, with superior thermodynamic properties, is well-established in industrial settings but remains unsuitable for small systems near the public due to toxicity.

### 3.4 Innovative System Configurations

A key contribution of this review is its articulation of how system design innovations can expand the viable refrigerant space. Microchannel heat exchangers, with refrigerant channels below 1 mm, dramatically reduce refrigerant charge and improve heat transfer performance. Secondary loop systems isolate hazardous refrigerants (such as ammonia) in machine rooms, enabling their use in public-facing applications such as supermarkets. Low-pressure refrigerant systems using centrifugal compressors can utilize high-critical-temperature HFOs with excellent efficiency. These system innovations shift the constraint framework, making previously impractical refrigerants viable through engineering design rather than chemistry alone.

Table 1: Overview of key refrigerant candidates reviewed by McLinden et al. (2020)

| Refrigerant | Type | GWP100 | ODP | ASHRAE Class | Primary Application |
|---|---|---|---|---|---|
| R-410A | HFC blend | 2,090 | 0 | A1 | AC systems (incumbent) |
| R-404A | HFC blend | 3,943 | 0 | A1 | Commercial refrigeration |
| HFO-1234yf | HFO | <1 | 0 | A2L | Automotive AC |
| HFO-1234ze(E) | HFO | <1 | 0 | A2L | Chillers, foam |
| HFO-1336mzz(Z) | HFO | 2 | 0 | A1 | Low-pressure chillers |
| HCFO-1233zd(E) | HCFO | 1 | <0.001 | A1 | Industrial chillers |

| | | | | | |
|---|---|---|---|---|---|
| R-32 (HFC-32) | HFC | 675 | 0 | A2L | AC, blend component |
| $CO_2$ (R-744) | Natural | 1 | 0 | A1 | Supermarkets, transport |
| $NH_3$ (R-717) | Natural | 0 | 0 | B2L | Industrial refrigeration |

## IV. STUDY 2 — DEVELOPMENT OF HFO-1123 MIXTURES AS R-410A REPLACEMENTS

Hashimoto et al. (2019), published in Science and Technology for the Built Environment, report the development of novel binary (HFO-1123/HFC-32) and ternary (HFO-1123/HFC-32/HFO-1234yf) refrigerant blends from AGC Chemicals (Japan) as alternatives to R-410A. The study is notable both for its systematic characterization approach and for the unique self-decomposition safety challenge associated with HFO-1123.

### 4.1 HFO-1123 — Challenges and Opportunities

HFO-1123 (trifluoroethylene, 1,1,2-trifluoroethene) has a near-zero GWP (< 1) and a normal boiling point of 214 K, slightly lower than R-410A's 222 K. Its critical temperature of 331.9 K is about 13 K lower than R-410A, meaning that at high condensing temperatures, HFO-1123 operates in a supercritical cycle. While its suction gas density (46.9 kg/m$^3$) is higher than both R-410A and HFC-32, giving it a high volumetric refrigerating capacity (111% of R-410A), its standalone COP is inferior due to its low critical point. Critically, pure HFO-1123 is subject to a disproportionation reaction ($CHF{=}CF_2 \rightarrow 1.5C + 0.5CF_4 + HF$, $\Delta H = -250$ kJ/mol) at elevated temperatures and pressures, which precludes its use as a pure refrigerant.

### 4.2Mixture Design and Temperature Glide

To address both the COP deficit and the safety concern, the researchers blended HFO-1123 with HFC- 32 and HFO-1234yf. A critical advantage of HFO-1123/HFC-32 mixtures is their very small temperature glide compared to other HFO/HFC-32 blends, due to the similar boiling points of HFO-1123 (214 K) and HFC-32 (222 K). The maximum temperature glide of HFO-1123/HFC-32 is only 1.8 K, versus 8.2 K for HFO-1234yf/HFC-32 and 14.1 K for HFO-1234ze(E)/HFC-32. A small temperature glide is essential for maintaining heat exchange efficiency in air-conditioning systems.

The addition of HFO-1234yf in the ternary blend reduces the vapor pressure from above R-410A levels (for the binary blend) to approximately R-410A equivalence, enabling use in existing equipment without pressure-related modifications. The ternary blend HFO-1123/HFC-32/HFO-1234yf (40/44/16 wt%) achieves near-azeotropic behavior and GWP100 < 298 (composition-dependent).

### 4.3 Self-Decomposition Safety Assessment

A critical contribution of this study is its rigorous experimental evaluation of HFO-1123 disproportionation under forced ignition conditions. Using an autoclave apparatus equipped with pressure and temperature sensors, the researchers demonstrated that while pure HFO-1123 undergoes disproportionation under ordinary compressor operating conditions, HFO-1123/HFC-32 blends with at least 40 wt% HFC-32 require pressures exceeding 14.9 MPa and temperatures above 570 K for propagation — conditions far outside normal air-conditioning operation.

The safety envelope was further evaluated under air contamination conditions. Counterintuitively, the presence of 1 mol% air elevated the threshold pressure and temperature required for disproportionation propagation compared to air-free mixtures. The authors postulate that oxygen reacts with HFO-1123 while nitrogen provides a dilution effect. This finding substantially strengthens the safety case for HFO- 1123-based blends in practical refrigeration applications.

### 4.4 Performance Validation

Drop-in testing on a 4 kW room air conditioner demonstrated that HFO-1123/HFC-32 (40/60 wt%) and the ternary blend achieved Annual Performance Factors (APF) of approximately 96% and 95% of HFC- 32, respectively. The compressor discharge gas temperature was lower than HFC-32 in cooling mode, indicating suitability for high compression ratio operation. Compatibility with POE oil (VG68) was confirmed, with no phase separation observed down to 213 K.

Table 2: Key properties of HFO-1123 mixtures vs R-410A reference (Hashimoto et al., 2019)

| Property<br>GWP100 | HFO-1123 (pure)<br>< 1 | Binary (40/60)<br>< 405 | R-410A (reference)<br>2,090 |
|---|---|---|---|
| Normal BP (K) | 214.0 | 216.8 | 221.8 |
| essure at 298K (kPa) | 2123 | 1967 | 1657 |
| Temperature glide (K) | 0 (pure) | 1.7 | 0.1 |
| capacity vs R-410A | 1.11 | 1.17 | 1.00 |
| e COP vs R-410A | 0.92 | 0.98 | 1.00 |
| Self-decomposition risk | High (normal ops) | Low (>14.9 MPa/570K) | None |
| APF vs HFC-32 (%) | N/A | ~96% | Comparable |

## V. STUDY 3 — DATA MINING FOR ENERGETIC AND EXERGETIC PERFORMANCE PREDICTION OF R457A AND R459B

Sahin and Yildirim (Journal of Thermal Analysis and Calorimetry, 2025) present a data mining approach to predict the thermodynamic performance of two new-generation HFO-blend refrigerants — R457A and R459B — considered as alternatives to R404A. Both carry GWP100 of approximately 139–143 and an A2L safety classification, positioning them as near-term compliant alternatives under the EU F-Gas Regulation (GWP < 150 threshold).

### 5.1 Refrigerant Characterization

R457A (R32/1234yf/R152a at 18/70/12 by mass) has a normal boiling point of -42.6°C, a critical temperature of 91.3°C, and a latent heat of vaporization of 215.18 kJ/kg at -7°C. R459B (R32/R1234yf/R1234ze(E) at 21/69/10 by mass) has a slightly lower boiling point of -45.0°C, critical temperature of 87.5°C, and latent heat of 204.17 kJ/kg. Both are ternary zeotropic blends incorporating HFO components and represent the compositional direction of next-generation commercial refrigerants leveraging HFO-1234yf as the dominant component for low GWP, with HFC-32 for thermodynamic performance and either R152a or HFO-1234ze(E) as modifiers.

### 5.2 Mathematical Modeling Framework

The refrigeration cycle was modeled using Engineering Equation Solver (EES) software with standard thermodynamic assumptions: cooling capacity of 1 kW, isentropic compressor efficiency of 70%, dead- state conditions of 101 kPa and 25°C. Evaporator temperatures ranged from -40°C to 5°C, condenser temperatures from 25°C to 45°C, with superheating and subcooling varied at 3, 5, 7, and 10°C. The energy analysis computed COP, mass flow rate, compressor work, and cooling capacity. The exergy analysis tracked irreversibilities at each component — compressor, evaporator, condenser, and expansion valve — and calculated second-law (exergy) efficiency.

### 5.3 Data Mining Methodology

Six machine learning models were implemented in WEKA 3.9 software: linear regression (LR), multilayer perceptron (MLP), M5 rules (M5R), M5P model tree (M5P), random committee (RC), and decision table (DT). The input variables were evaporator temperature, condenser temperature, superheating temperature increment, and subcooling temperature increment. Outputs were COP and second-law exergy efficiency. The dataset comprised the EES simulation results, partitioned for training and validation. Model performance was evaluated using three metrics: coefficient of determination (R2), mean absolute error (MAE), and root mean square error (RMSE).

### 5.4 Results — MLP Model Supremacy

The multilayer perceptron emerged as the best-performing model across all metrics and both refrigerants. For R457A, MLP achieved R2 = 0.9997 for COP and R2 = 0.9984 for exergy efficiency prediction. For R459B, the values were R2 = 0.9994 (COP) and R2 = 0.9989 (exergy efficiency). All other models showed substantially lower R2 values, particularly linear regression, confirming the inherently nonlinear relationship between operating temperatures and thermodynamic performance in subcooled/superheated refrigeration cycles. The MAE values for COP prediction using MLP were below 0.03 for both refrigerants, while for exergy efficiency prediction, MAE was below 0.003. The maximum percentage error for COP across all test conditions was 3.043% (R457A) and 3.317% (R459B), while for exergy efficiency the maxima were3.265% and 2.307% respectively. These error levels are well within engineering acceptability for rapid screening applications.

Table 3: Data mining model performance for R457A and R459B (Sahin & Yildirim, 2025)

| Metric | R457A COP | R457A ηII | R459B COP | R459B ηII |
|---|---|---|---|---|
| R2 (MLP) | 0.9997 | 0.9984 | 0.9994 | 0.9989 |
| MAE (MLP) | < 0.03 | < 0.003 | < 0.03 | < 0.002 |
| RMSE (MLP) | < 0.04 | < 0.003 | < 0.04 | < 0.003 |
| Max % error | 3.043% | 3.265% | 3.317% | 2.307% |
| Best model | MLP | MLP | MLP | MLP |

### 5.5 Thermodynamic Insights

Both refrigerants exhibit the expected inverse relationship between condenser temperature and COP/exergy efficiency. At evaporator temperature of 0°C with 5°C superheating and subcooling, R457A achieves COP values from approximately 8 (Tc = 25°C) down to about 3 (Tc = 45°C). R459B shows similar trends with slightly lower absolute values at low evaporator temperatures, reflecting its lower critical temperature. Exergy efficiency declined with rising condenser temperature for both, confirming that elevated heat rejection temperatures amplify system irreversibilities. The closeness of MLP-predicted values to EES-calculated actuals across all conditions confirms the generalizability of the neural network model.

## VI. STUDY 4 — SYNERGY ANALYSIS OF ALTERNATIVE REFRIGERANTS FOR REFRIGERATING TRANSPORT

Huminic and Huminic (International Journal of Low Carbon Technologies, 2008) develop a theoretically rigorous framework — synergy analysis — for computing the vaporisation heat of refrigerants from first principles, connecting macroscopic thermodynamic quantities with molecular-level statistical mechanics via a parameter called the coupling ratio. The work is validated against four transport refrigerants: R22, R502, R404A, and R410A.

### 6.1 Theoretical Foundation

The central contribution is a closed-form expression for the specific thermal effect of an isobar-isothermal process (vaporisation heat), derived by combining classical thermodynamics with statistical entropy formulations. Starting from the general energy balance and applying the Planck/Boltzmann entropy equation (equivalently Shannon's information entropy), the authors derive the specific vaporisation heat as:

$$lV = (kNT/M)(1+\beta)\ \ln(v''/v') + p(v'' - v')$$

where $\beta$ (coupling ratio) = $(N'' - N')/N$ is the order parameter linking molecular association/dissociation to the phase change

This formulation identifies three components of vaporisation heat: an entropy-of-expansion term, a molecular association/dissociation term (governed by β), and a mechanical work term. This is a notable advance over the Clapeyron equation, which while commonly used, is not a closed form and requires knowledge of dp/dT.

### 6.2 The Coupling Ratio as Order Parameter

The coupling ratio β serves as a bridge between macroscopic phase behavior and molecular microstructure. A positive β corresponds to dissociation (vaporisation), while negative β corresponds to association (condensation). Assuming saturated vapors contain no associated molecules and liquid phase molecules exist as triplets (consistent with laminar flow in fluid mechanics), the average coupling ratio evaluates to $\beta_{ave} = 0.667$. This value was used in the vaporisation curve calculations for all four studied refrigerants.

At the critical state, the coupling ratio takes the value $\beta C = -(1 + MpCvC/RTC)$. Using Van der Waals equation, $\beta C \approx -1.375$. For the four studied refrigerants, the computed critical coupling ratios fall in the narrow interval $-1.492 < \beta C < -1.264$, confirming the generality of the formulation. The dependence of TC/M on critical state variables simplifies to an approximately linear (quasi-Boyle) relationship: $TC/M \cong C \cdot pCvC/R$.

### 6.3 Magnetic Analogy and Critical State Phenomena

A particularly innovative aspect of the work is the establishment of an analogy between liquid-vapor critical phenomena and magnetic phase transitions (the Ising model for ferromagnetism). At the critical state, liquid polarization doubles the number of distinct components from N to N' = 2N, while vapor association reduces them to N'' = N/2, yielding a critical coupling ratio of $\beta K = -1.5$ — in the centre of the calculated interval. This analogy with the Curie temperature of ferromagnetic materials explains the anomalous behavior of heat conductivity, heat diffusivity, and specific heat observed experimentally near the critical state, attributing them to molecular coupling processes.

### 6.4 Experimental Validation

The vaporisation curves (saturation pressure vs. temperature) calculated using the synergy method were compared against experimental data and Clapeyron equation predictions for R22, R502, R404A, and R410A in the temperature range 223–313 K. The synergy-calculated values showed excellent agreement with experimental data, with deviations generally below 5% across most of the temperature range. The Clapeyron equation showed comparable accuracy at intermediate temperatures but diverged more at temperature extremes, particularly for R404A and R410A. The synergy formulation offers the practical advantage of being a closed-form expression requiring only critical parameters and the coupling ratio.

Table 4: Synergy analysis critical parameters and validation deviations for transport refrigerants (Huminic & Huminic, 2008)

| Refrigerant | M (g/mol) | TC (K) | pC (MPa) | βC (calc.) | Max deviation (%) |
|---|---|---|---|---|---|
| R22 (HCFC-22) | 86.47 | 369.28 | 4.99 | ~-1.28 | ~2.2 |
| R502 (blend) | 111.6 | 355.35 | 4.07 | ~-1.38 | ~2.5 |
| R404A (blend) | 97.6 | 345.27 | 3.74 | ~-1.49 | ~5.1 |
| R410A (blend) | 72.6 | 344.5 | 4.90 | ~-1.26 | ~3.9 |

## VII. CROSS-CUTTING THEMES AND SYNTHESIS

### 7.1 Compositional Continuity Across Studies

A striking feature of reading these four studies together is the compositional continuity in refrigerant development. HFO-1234yf — the dominant component of R457A and R459B (Study 3, ~70% by mass), a significant component in the HFO-1123 ternary blend (Study 2), and the leading automotive AC refrigerant reviewed by McLinden et al. (Study 1) — emerges as the central molecule in the HFO transition. Its combination of very low GWP, acceptable safety classification (A2L), and good thermodynamic properties makes it a near-universal building block for next-generation refrigerant blends. HFC-32 appears as a performance enhancer in both the HFO-1123 binary blend (Study 2) and as a component of R457A and R459B (Study 3), consistent with its role as reviewed by McLinden et al.

### 7.2 The Flammability-GWP Trade-off

All four studies either address or implicitly acknowledge the fundamental tension between low GWP and flammability. McLinden et al. most explicitly articulate this: higher fluorine substitution reduces flammability but increases GWP. The result is that virtually all competitive low-GWP candidates carry at least a 2L (mildly flammable) classification. The HFO-1123 work (Study 2) adds a third dimension

— self- decomposition — as a unique safety hazard for that molecule, addressed through blend formulation. R457A and R459B (Study 3) are A2L, requiring system-level safety measures that will become standard in the industry. The synergy analysis (Study 4) provides tools to characterize the phase behavior of these blends more efficiently, supporting safety envelope calculations.

### 7.3 The Role of Computational Tools

A clear progression in analytical methodology is observable across the four studies. Huminic and Huminic (2008) establish a first-principles thermodynamic framework requiring only critical parameters. Hashimoto et al. (2019) employ REFPROP 9.1 with custom equations of state for property calculations. McLinden et al. (2020) synthesize systematic computer searches across thermodynamic parameter spaces. Sahin and Yildirim (2025) represent the frontier: machine learning replacing full thermodynamic simulation for performance prediction with R2 > 0.999 accuracy. The trajectory is clear — as blend complexity increases (three-, four-component zeotropic mixtures with composition-dependent properties), purely analytical approaches become computationally prohibitive, and data-driven methods offer practical alternatives.

### 7.4 Limitations Across Studies

Table 5: Limitations and suggested future directions for each reviewed study

| Study | Key Limitations | Future Research Directions |
|---|---|---|
| McLinden et al. (2020) | Review scope; fast-evolving field; TFA degradation products lack consensus | Long-term TFA accumulation studies; system economics at scale; novel cycle architectures |
| Hashimoto et al. (2019) | Equipment optimized for HFC-32, not for new blends; limited APF evaluation scenarios | Dedicated equipment optimization; long- term stability testing; field deployment data |
| Sahin & Yildirim (2025) | Theoretical only (EES-generated data, no experiments); single-stage cycle; fixed compressor efficiency | Experimental validation; two-stage cycles; variable efficiency compressors; more HFO blends |
| Huminic & Huminic (2008) | Older refrigerants validated (R22/R502 phased out); deviations increase near critical point | Extension to HFO blends; multi-component mixtures; supercritical regime validation |

## VIII. DISCUSSION

### 8.1 Industrial and Policy Implications

The four studies, read together, present a coherent picture of an industry in purposeful transition. McLinden et al. provide the regulatory and technical road map. Hashimoto et al. demonstrate that the road map is being followed at the laboratory scale, with serious attention to the safety challenges unique to each candidate molecule. Sahin and Yildirim show that performance evaluation can now be accelerated dramatically through machine learning, enabling rapid screening of the thousands of possible blend formulations that the HFO chemical space offers. Huminic and Huminic provide a unifying thermodynamic language for characterizing these candidates from fundamental principles.

For the commercial refrigeration sector (supermarkets, cold chains, industrial cooling), the phase-out of R404A is the most pressing near-term challenge. R457A and R459B, with GWP values just below the 150 threshold of the EU F-Gas Regulation, represent credible interim solutions. Their COP and exergy performance, as demonstrated by the data mining analysis, is competitive with R404A. Combined with the non-flammable R471A characterized in other recent literature, the commercial refrigeration sector has a widening portfolio of options.

For the air-conditioning sector, the R-410A replacement challenge is more complex, as McLinden et al. document extensively. The HFO-1123 blends developed by Hashimoto et al. represent one promising pathway, delivering near-R-410A capacity and COP while drastically reducing GWP, albeit with residual mild flammability and equipment pressure design considerations. The parallel developments in low- pressure centrifugal chiller refrigerants (HFO-1336mzz, HCFO-1233zd) offer alternative paths for large commercial cooling.

### 8.2 The Emerging Role of Artificial Intelligence

The data mining results of Sahin and Yildirim mark an important methodological advance with implications beyond refrigerant performance prediction. As the refrigerant candidate space expands — driven by the recognition that no single ideal replacement exists and that tailored blends will be required for different applications — the experimental and computational effort required for comprehensive characterization grows combinatorially. Machine learning models trained on thermodynamically modeled datasets can serve as rapid pre-screening tools, directing experimental effort toward the most promising candidates. The MLP's ability to capture the nonlinear, multi-input structure of refrigeration system thermodynamics with R2 > 0.999 accuracy positions it as a potentially transformative tool for refrigerant development workflows.

### 8.3 Environmental Caveats

McLinden et al. raise an important concern that the other studies do not address: the atmospheric breakdown products of HFOs. The -CF3 group present in HFO-1234yf, HFO-1234ze(E), and related molecules generates trifluoroacetic acid (TFA) as an atmospheric degradation product. TFA is water-soluble, toxic to aquatic organisms, and effectively non-biodegradable. While current TFA concentrations from HFO sources are below concerning levels, the long-term accumulation in closed water bodies lacking ocean drainage is a potential concern as HFO deployment scales globally. This deserves attention in future environmental impact assessments of next-generation refrigerants.

## IX. CONCLUSION

This review has synthesized four peer-reviewed contributions to the rapidly evolving science of next-generation refrigerants. The principal conclusions are:

- The refrigerant transition from high-GWP HFCs is irreversible and regulated: the Kigali Amendment and regional F-Gas frameworks mandate an 85% reduction in GWP-weighted production, driving the shift to HFOs and HFO-based blends across all major applications (McLinden et al., 2020).
- HFO-1123 binary and ternary blends demonstrate near-R-410A performance with GWP100 < 300-400, small temperature glide (< 1.8 K), and confirmed safety under realistic compressor conditions — the disproportionation hazard can be effectively managed through blend composition with minimum 40 wt% HFC-32 (Hashimoto et al., 2019).
- Data mining, specifically the multilayer perceptron model, achieves R2 > 0.999 in predicting both COP and second-law efficiency of new HFO-blend refrigerants R457A and R459B, offering a powerful, computationally efficient alternative to full thermodynamic simulation for rapid performance screening (Sahin & Yildirim, 2025).
- Synergy analysis provides a closed-form thermodynamic framework for computing vaporisation heat from critical state parameters, validated for R22, R502, R404A, and R410A, and readily extensible to next-generation blends — offering advantages over the Clapeyron equation particularly at temperature extremes (Huminic & Huminic, 2008).
- HFO-1234yf and HFC-32 emerge as the compositional building blocks of most near-term low- GWP blend solutions, appearing across studies as dominant components in both R-410A and R404A replacement refrigerants.
- The field requires integrated advancement across

four dimensions simultaneously: new chemical formulations, safety validation, AI-driven prediction tools, and fundamental thermodynamic frameworks — no single approach is sufficient for the complexity of the transition underway.

As the refrigeration industry navigates this generational transition, the insights from these four studies collectively confirm both the urgency and the tractability of the challenge. The scientific tools — from closed-form thermodynamic equations to neural networks — and the chemical toolkit — from HFO-1123 blends to ternary HFO mixtures — are advancing in parallel, charting a credible path toward a lower- GWP refrigeration future.

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