ENHANCING sCO$_2$ BRAYTON POWER CYCLE EFFICIENCY IN COLD AMBIENT CONDITIONS THROUGH WORKING FLUID BLENDS

Abstract

Supercritical carbon dioxide (sCO$_2$) recompression Brayton cycles are promising for high-efficiency energy conversion due to their compactness and favorable thermophysical properties. However, their performance is limited in cold environments because pure CO$_2$ has a relatively high critical temperature (31 °C), leading to phase instability and operational challenges at low compressor inlet temperatures (CIT).

This study investigates the performance benefits of blending CO$_2$ with low-critical-temperature additives—Methane (CH$_4$), Tetrafluoromethane (CF$_4$), Nitrogen Trifluoride (NF$_3$), and Krypton (Kr)—to form alternative working fluids better suited for sub-zero conditions. Using detailed thermodynamic simulations, we analyze how these mixtures affect cycle efficiency, compressor work, optimal pressure levels, and recuperator behavior across a wide range of additive concentrations and heat exchanger conductance values (UA).

Results show that high-additive mixtures (50–90 mol%) significantly lower the working fluid's critical temperature, enabling fully supercritical operation down to –40 °C CIT and below. This leads to thermal efficiency improvements of up to 10 percentage points over pure CO$_2$ cycles. CH$_4$- and CF$_4$-rich mixtures exhibited the highest efficiency gains, while NF$_3$ also showed strong performance at moderate sub-zero conditions. Kr mixtures provided modest but consistent improvements. Additionally, the mixtures allowed for lower optimal compressor inlet pressures (down to ~3.8 MPa), reduced specific compressor work, and enhanced turbine expansion ratios.

The performance gains were most pronounced when sufficient UA was available to avoid pinch-point limitations in the low-temperature recuperator (LTR), especially for cold-end heat recovery. Simulation results confirmed that the LTR became the limiting component in high-efficiency configurations, and optimal UA distribution shifted toward increased LTR capacity for mixture-based cycles.

These findings demonstrate that CO$_2$-based fluid blends can extend the operational range and efficiency of recompression Brayton cycles in cold climates, offering a practical pathway to robust low-temperature energy conversion.

1. Introduction

Supercritical carbon dioxide (sCO_2) Brayton power cycles have gained significant attention in recent decades as a promising alternative to conventional steam Rankine cycles for power generation [1,2,3,4,5,6]. By operating the working fluid above its critical point (critical temperature $\approx$31°C, critical pressure $\approx$7.4 MPa), sCO_2 cycles can achieve high thermal efficiencies (often exceeding 50% at moderate turbine inlet temperatures) [1]. They also feature a compact turbomachinery size and high power density, owing to the high fluid density in the supercritical state [3]. These advantages make sCO_2 systems attractive for a range of applications, including next-generation nuclear reactors [1,3], concentrated solar power (CSP) plants [7,8], and waste heat recovery in industrial processes [9,10]. In particular, the sCO_2 Brayton cycle's efficiency remains high even at the intermediate heat source temperatures of advanced nuclear and CSP systems, and the simpler single-phase circuit enables potentially lower cost and smaller footprints than water–steam cycles [3,7,9]. The technology has been extensively reviewed in the literature [3,4,5,6], and several pilot and demonstration projects are underway to validate its performance in practice [11,12]. However, despite these strengths, certain operational challenges must be addressed before sCO_2 cycles can realize their full potential across all conditions.

One key challenge arises from the thermophysical characteristics of CO_2 near its critical point. The performance of an sCO_2 cycle is highly sensitive to the temperature and pressure at the cold end of the cycle (condenser/cooler and compressor inlet). In theory, lowering the compressor inlet temperature should increase the cycle's pressure ratio and thermal efficiency, analogous to how a colder sink boosts a Rankine cycle's efficiency. In practice, however, CO_2's relatively high critical temperature (~31°C) imposes a limit on how much the sink temperature can be reduced [13]. If the ambient heat rejection temperature falls near or below 31°C, the CO_2 in the cooler will approach two-phase conditions, risking condensation or unstable operation at the compressor inlet. Most sCO_2 systems are therefore designed to maintain the cooler outlet (compressor inlet) just above the critical temperature (typically 32–35°C) to avoid crossing into the two-phase region [13,14]. This means that in cold ambient environments – for example, locations with sub-freezing air temperatures or applications with a very low-temperature heat sink – a conventional sCO_2 Brayton cycle cannot fully capitalize on the cold sink without risking condensation. The net result is a performance penalty in cold conditions: the cycle cannot be optimally cooled, and the compressor may not realize the reductions in work that a colder inlet would otherwise allow. In short, whereas high ambient temperatures (e.g. 40–50°C in desert climates) are known to degrade sCO_2 cycle efficiency by forcing a higher compressor inlet temperature [13], very low ambient temperatures present the opposite problem of CO_2's phase limitations, effectively constraining the minimum compressor inlet temperature and forfeiting potential efficiency gains. This issue stemming from CO_2's critical-point proximity represents a significant knowledge gap for deploying sCO_2 cycles in cooler climates or in applications with seasonal ambient swings.

A promising approach to overcome this thermodynamic constraint is to modify the working fluid itself via binary mixtures. Rather than using pure CO_2, the working fluid can be blended with a secondary component to tailor the fluid's critical properties and overall performance [14,3]. By adjusting the mixture composition, it is possible to shift the critical point of the working fluid and alter its thermal behavior in the cycle. This concept is analogous to refrigerant blending in HVAC applications and has precedent in power cycles as well: helium–xenon mixtures have been used in closed Brayton cycles to optimize turbomachinery performance [14], and ammonia–water mixtures in Kalina cycles exploit variable boiling properties to improve heat recovery [14]. In the context of sCO_2 power systems, research in the past decade has increasingly explored CO_2-based binary mixtures as a means to enhance cycle efficiency or extend operability beyond the limits of pure CO_2 [15,16]. Several reviews and comparative studies have categorized CO_2 mixture strategies alongside other cycle improvements [14,3,7,17], underscoring that working-fluid composition adjustment is now recognized as a viable route for performance enhancement.

Early investigations into CO_2-based mixtures for power cycles demonstrated the potential benefits and trade-offs of this approach. For instance, researchers at Sandia National Laboratories conducted one of the first mixture studies on a supercritical CO_2 loop, examining the effect of adding small amounts of various gases (e.g. SF_6, CH_4, N_2, neon, n-butane) on a 50 kW sCO_2 compressor's performance [18]. Around the same time, Jeong et al. [19,20,21] in Korea introduced the idea of tuning CO_2's critical point for better cycle integration with a sodium-cooled fast reactor, by blending CO_2 with select gases. They tested five candidate additives spanning a range of critical temperatures – namely cyclohexane, n-butane, isobutane, propane, and hydrogen sulfide (H_2S) – and found that among these, the CO_2/H_2S mixture yielded the highest cycle thermal efficiency [19,20,21]. (H_2S, being a "heavier" component with a critical temperature around 100°C, effectively raises the working fluid's critical point, enabling a partial condensation in the cycle and thereby reducing compression work through liquid pumping in a transcritical process.) On the other hand, CO_2/propane mixtures were noted to offer superior heat transfer performance and lower pressure drops in heat exchangers [22], owing to propane's favorable thermophysical properties, even if their impact on cycle efficiency was less pronounced than H_2S. These studies suggested that properly chosen additives can improve various aspects of cycle performance, but the optimum choice may depend on whether one prioritizes maximum efficiency or other factors like heat transfer and pressure drop.

More recently, attention has focused on high-critical-temperature additives that deliberately allow condensation at the compressor inlet to boost efficiency. One notable example is the use of titanium tetrachloride ($TiCl_4$) as a CO_2 co-fluid. $TiCl_4$ has an extremely high critical temperature (around 365°C) and was proposed as a means to create a transcritical CO_2 cycle that operates more like a Rankine cycle with a liquid pump. Computational studies by Bonalumi et al. [23] and experimental assessments by Invernizzi et al. [24] showed that adding a small fraction of $TiCl_4$ to CO_2 can increase the cycle's efficiency by several percentage points. In fact, a CO_2–

TiCl$_4$ blend was reported to improve Brayton cycle efficiency by up to ~5.5% absolute compared to pure CO$_2$ [23,24]. Moreover, such heavy-fluid blends were found to mitigate performance degradation under high ambient temperatures: by raising the critical point well above ambient, the cycle can condense and reject heat more effectively even on hot days, avoiding the steep efficiency drop-off pure CO$_2$ experiences at high sink temperatures [16]. These findings reinforce the idea that altering the working fluid composition can be a powerful tool to tailor cycle behavior to different operating regimes. Overall, optimized CO$_2$-based mixtures have been shown to either increase peak efficiencies or maintain higher efficiencies over a wider range of ambient conditions than the standard pure-CO$_2$ cycle [15,16]. In other words, mixtures provide an extra degree of freedom in cycle design, potentially extending the operational envelope into conditions that pure CO$_2$ cannot handle as efficiently.

Despite the growing body of work on CO$_2$ mixtures, the majority of studies to date have emphasized heavier additives aimed at high-temperature or high-ambient applications. These heavy additives (with higher critical temperatures than CO$_2$) enable cycle architectures that include partial condensation, and they tend to yield benefits when the ambient heat sink is relatively warm or when the goal is to maximize absolute efficiency via recuperation and liquid pumping [23,24,16]. In contrast, far less attention has been given to the converse strategy: using low-critical-temperature additives to improve cycle performance in cold ambient conditions. Lighter gases (with lower critical temperatures than CO$_2$) can depress the critical point of the working fluid mixture, theoretically allowing the cycle to remain supercritical even at much lower sink temperatures. Intuitively, this approach could unlock higher efficiencies in cold environments, since the cycle could operate with a much lower compressor inlet temperature (fully supercritical, single-phase) without encountering two-phase issues. However, previous investigations into light additives have been limited and somewhat inconclusive. In some cases, adding a non-condensable light gas like helium or neon had negligible or even slight negative effects on cycle efficiency at design conditions [16]. For example, Vesely et al. found that small admixtures of low-boiling gases (He, Ar, etc.) provided minimal efficiency improvement in a recompression cycle, primarily affecting the cycle only under off-design scenarios [25,26]. Similarly, a study at Sandia reported only modest changes in compressor behavior with a few mole percent of methane or neon added, compared to the more pronounced improvement seen with heavier SF$_6$ doping [18]. These outcomes suggest that while light additives can indeed lower the critical temperature, they do not automatically guarantee a better performance unless the operating conditions strongly demand that shift. In other words, the magnitude of benefit likely depends on how far the ambient/cooling conditions deviate below CO$_2$'s natural critical point [16]. It has been posited that the colder the environment (relative to 31°C), the more significant the efficiency gains a suitably tailored low-critical-point mixture could achieve [16]. This hypothesis, though compelling, remains to be thoroughly tested. To date, there has been no comprehensive study focusing on optimizing sCO$_2$ cycle performance specifically for very cold ambient temperatures using light-component mixtures.

Most mixture research has targeted improving the base cycle or hot-day operability, leaving a gap in knowledge regarding cold-day or cold-climate operation.

The present study seeks to address this gap by systematically exploring CO_2-based binary mixtures with low-critical-temperature additives as a strategy to enhance recompression Brayton cycle performance in cold ambient conditions. In particular, we focus on four candidate additives – methane (CH_4), nitrogen trifluoride (NF_3), carbon tetrafluoride (CF_4), and krypton (Kr) – which were selected for their markedly lower critical temperatures compared to CO_2. All four substances have critical temperatures well below 0°C [27,28,29,30].

Of course, introducing new working fluids also entails practical considerations, particularly with respect to safety and environmental impact. Some prior studies have highlighted the importance of accounting for environmental factors when evaluating alternative working fluids [31,32]. In the present case, each of the candidate additives comes with certain caveats. CH_4 is combustible and has a moderate global warming potential (GWP) as a greenhouse gas, although its atmospheric lifetime is relatively short. NF_3 and CF_4 are chemically inert in the cycle; however, both are extremely potent greenhouse gases if released. (For example, NF_3 has an atmospheric 100-year GWP on the order of 17,200 times that of CO_2, and CF_4 around 7,390 times that of CO_2 [33,34].) These values are many times higher even than CO_2 or CH_4, meaning that even a small leakage of NF_3 or CF_4 could offset the CO_2 emissions savings from efficiency gains. Krypton is an inert noble gas with no toxicity or flammability concerns; it has essentially zero direct GWP since it does not absorb infrared radiation. However, krypton is a rare constituent of air (approximately 1 ppm by volume) and is expensive to procure in large quantities. The use of Kr on an industrial scale would require gas separation infrastructure and careful economic consideration. In light of these issues, the present study not only evaluates the thermodynamic performance of CO_2-based cold-climate mixtures, but also discusses the environmental implications and practical viability of each blend. By examining both efficiency gains and potential environmental costs, we aim to identify which (if any) of these CO_2–based binary mixtures offer a meaningful performance improvement in cold ambient conditions and a reasonable trade-off in terms of safety and sustainability. The results and insights from this work will help guide the development of sCO_2 Brayton power cycles that can operate efficiently across a broader range of ambient temperatures, including extremely cold environments that were previously considered challenging for pure-CO_2 systems.

2. Methodology

2.1. Cycle Configuration

A recompression Brayton cycle with supercritical CO_2 as the baseline working fluid was modeled [X, X]. The cycle includes: a low-temperature (LT) recuperator and a high-temperature (HT) recuperator, a main compressor and a recompressor, a primary heat source that raises the fluid temperature prior to expansion in a turbine and a cooler that lowers the fluid temperature and pressure after expansion and recuperation, before compression.

The recompression fraction was optimized to maximize net cycle efficiency. The pinch points in the LT and HT recuperators were monitored to ensure sufficient temperature differentials for effective heat exchange. The total heat transfer conductance (UA) of each recuperator was set based on design constraints.
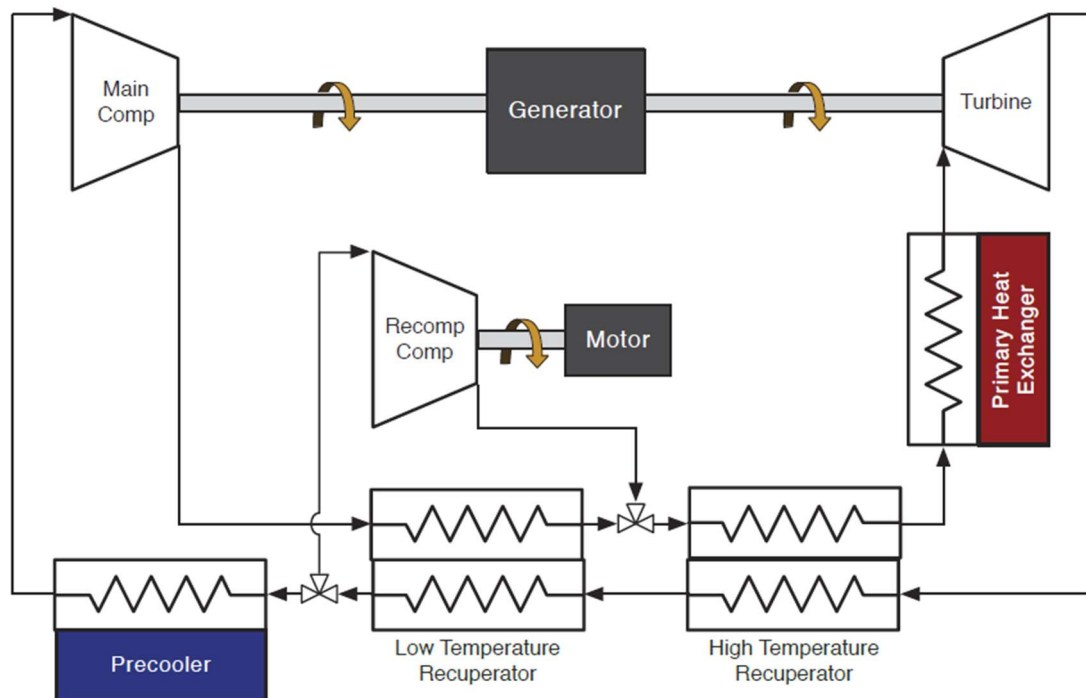

Figure 1: Recompression Brayton Power Cycle.

2.2. Blends Properties

The performance of supercritical CO_2 Brayton cycles is highly sensitive to the thermophysical properties of the working fluid, particularly near the critical point. This section presents a comparative analysis of four binary mixtures—CO_2–Kr, CO_2–CF_4, CO_2–CH_4, and CO_2–NF_3—selected for their potential to tailor critical properties and improve cycle performance in cold ambient or high-efficiency scenarios. All mixture properties were computed using REFPROP v10, and polynomial regressions were applied to experimental and simulated data to evaluate trends as a function of molar composition.

Table X summarizes the critical temperature, critical pressure, and critical density of pure components used in the binary mixtures:

Table X. Pure Fluids used for mixing with sCO_2

Working Fluid	Critical Temperature (K)	Critical Pressure (kPa)	Critical Density (Kg/m3)
CO_2	304.13	7377.3	467.60
NF_3	234	4460.7	562.47
CF_4	227.51	3750	625.70
Kr	209.48	5525	909.21
CH_4	190.56	4599.2	162.66

Each additive fluid has a significantly lower critical temperature than CO_2, while critical pressures and densities vary depending on the molecular structure and polarity. The goal of binary mixing is to reduce the pseudo-critical temperature of the resulting blend, shifting it downward to better match cold heat sink conditions without excessively raising compression power.

The variation of critical properties with molar concentration of the additive species was systematically modeled, as shown in Figures X–Y (from attached graphs). For each binary pair, the critical temperature (T_c), critical pressure (P_c), and critical density (ρ_c) evolve nonlinearly with mixture composition.

(a) CO_2–CF_4

The addition of tetrafluoromethane (CF_4) to CO_2 leads to a pronounced decrease in critical temperature, following the empirical cubic trend:

$$T_c(x_{CF_4}) = 7 \times 10^{-5}x^3 - 0.0064x^2 - 0.8772x + 305.35$$

with Tcr in Kelvin and x the molar percentage of CF_4. The critical pressure shows a quartic dependency:

$$P_c(x_{CF_4}) = -8 \times 10^{-5}x^4 + 0.0307x^3 - 3.3408x^2 + 72.588x + 7254.1$$

This mixture enables significant control over Tcr without dramatic depressurization, making it ideal for colder ambient integration or desalination hybrid systems.

(b) CO$_2$–CH$_4$

The methane blend exhibits an even stronger effect on Tcr reduction and a complex fourth-order pressure curve:

$$T_c(x_{CH_4}) = 7 \times 10^{-5}x^3 - 0.0125x^2 - 0.5583x + 303.14$$

Due to methane's low critical density (162.66 kg/m^3), the mixture leads to decreased overall fluid density, potentially impacting turbomachinery sizing and heat exchanger compactness.

and a complex fourth-order pressure curve:

$$P_c(x_{CH_4}) = 3 \times 10^{-4}x^4 - 0.0594x^3 + 2.1202x^2 + 19.532x + 7784.4$$

Due to methane's low critical density (162.66 kg/m^3), the mixture leads to decreased overall fluid density, potentially impacting turbomachinery sizing and heat exchanger compactness.

(c) CO$_2$–NF$_3$

Nitrogen trifluoride offers a balanced modulation of both critical temperature and density, with a relatively mild pressure penalty.

$$T_{cr}(x) = 6 \times 10^{-5}x^3 - 0.0045x^2 - 0.8501x + 305.56$$

The critical pressure decreases with a high-order polynomial fit:

$$P_{cr}(x) = -0.0001x^4 + 0.0384x^3 - 8.5323x^2 + 73.892x + 7309.6$$

(d) CO$_2$–Kr

Krypton, a noble gas, induces the highest increase in critical density while lowering the critical temperature and pressure in a predictable nonlinear manner:

$$T_c(x_{Kr}) = -6 \times 10^{-5}x^3 + 0.0106x^2 - 1.8884x + 309.4$$

$$P_c(x_{Kr}) = -2 \times 10^{-4}x^4 + 0.0469x^3 - 3.3563x^2 + 71.841x + 7326.2$$

High-density CO$_2$–Kr mixtures are advantageous for reducing component size and increasing recuperator density ratios, though thermal conductivity effects must be considered.
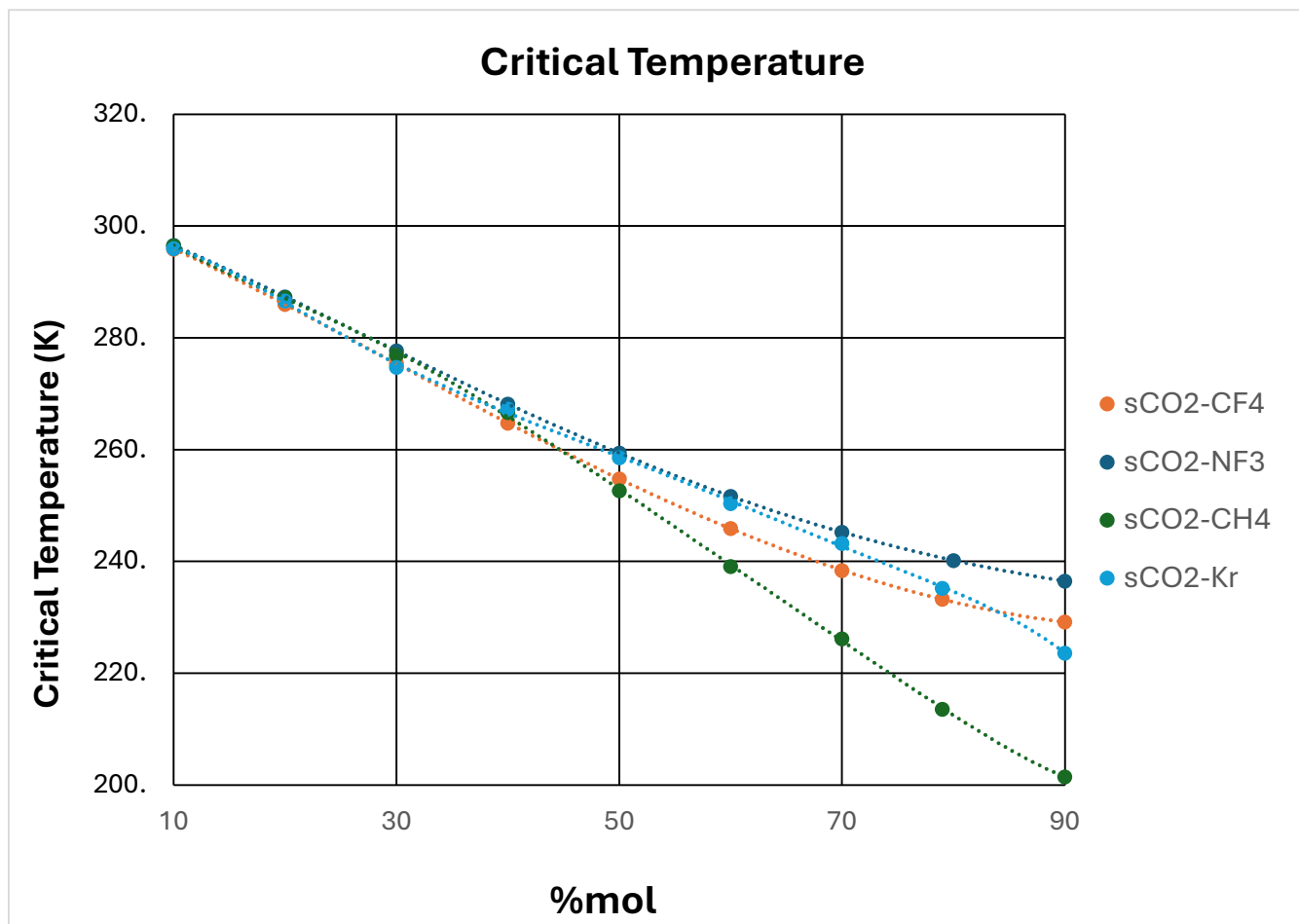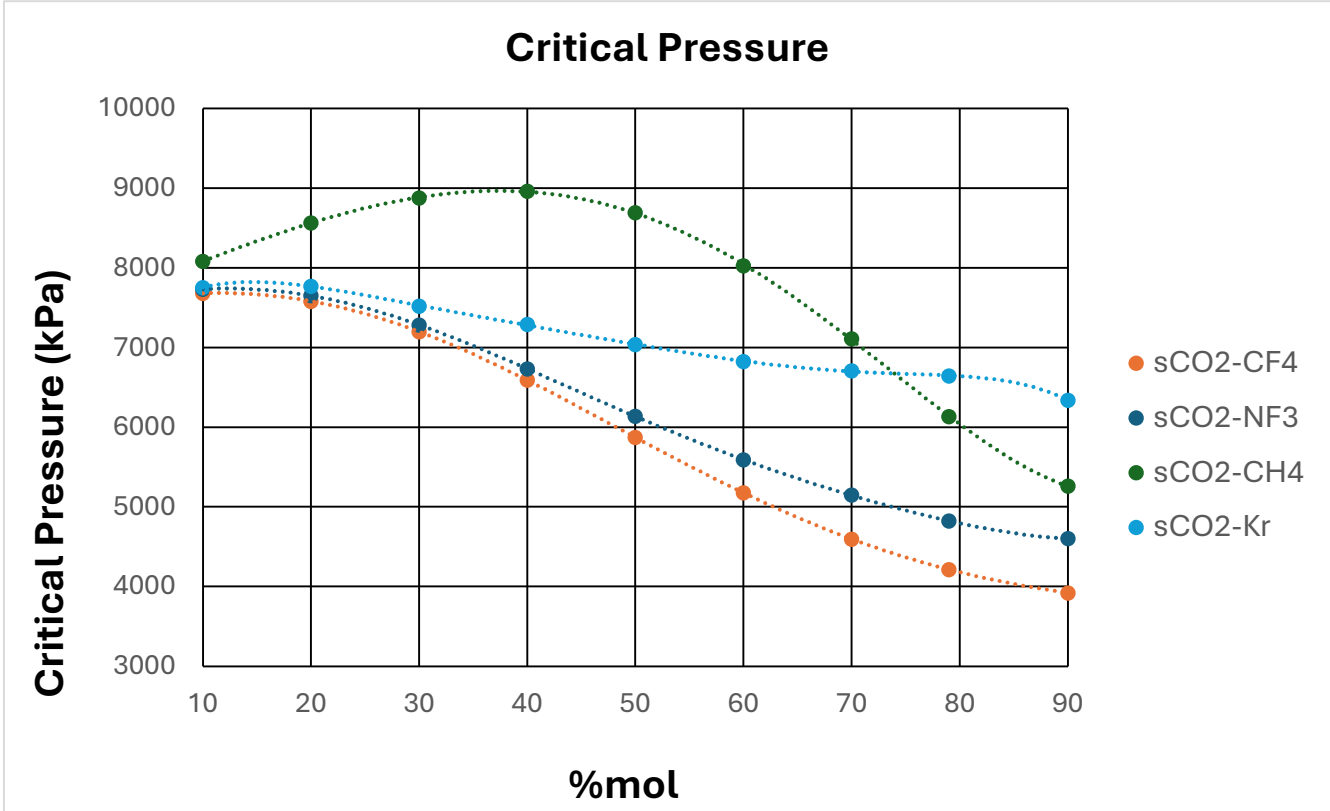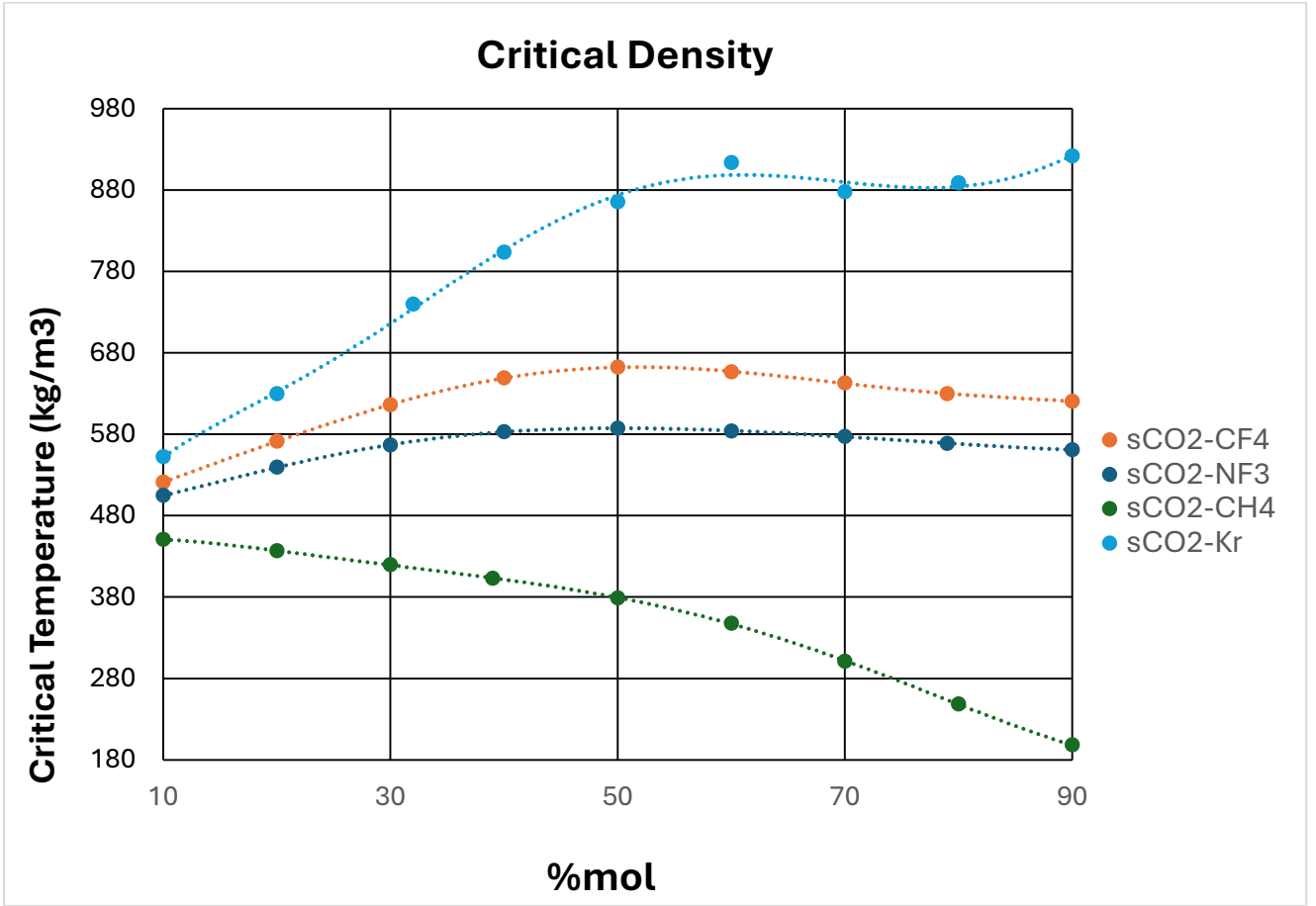
Figure 2:

Figure 3:

Figure 4:

Figure 5:

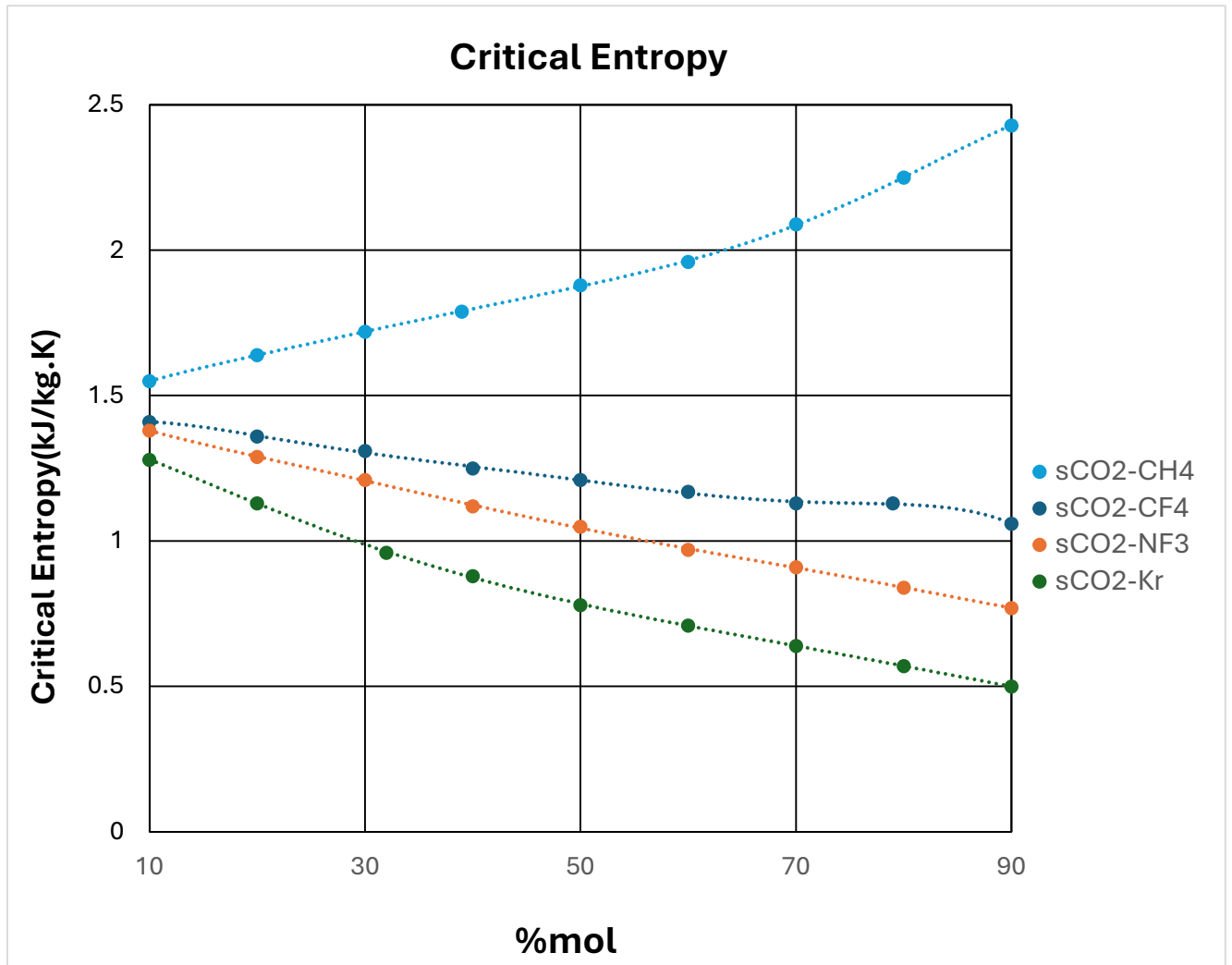## 2.3. Thermodynamic Modeling

A recompression sCO_2 Brayton cycle was thermodynamically modeled to assess performance under cold ambient conditions [35, 36]. The cycle includes a main compressor, a recompressor, a single turbine, two recuperative heat exchangers (a low-temperature recuperator, LTR, and a hightemperature recuperator, HTR), and a precooler (gas cooler) in a closed-loop configuration . Highside and low-side pressures were fixed based on design values, and the flow split to the recompressor was optimized to maximize net cycle efficiency. In the steady-state model, pressures, temperatures, and mass flow rates at all key state points (compressor inlets/outlets, turbine inlet/outlet, recuperator interfaces, etc.) are solved by applying energy balances and isentropic relations to each component.

To obtain accurate thermophysical properties at all states, NIST REFPROP v10 (Reference Fluid Properties database) was integrated with the model [37]. REFPROP v10 provides high-accuracy equations of state for pure CO_2 and mixtures, yielding reliable values of density, enthalpy, entropy, specific heats, and other properties over the relevant range of pressures and temperatures. By using REFPROP's real-fluid property evaluations, the modeling captures real-gas effects especially in the near-critical region and for non-ideal gas mixtures. This ensures that phenomena such as property variation

at low temperatures and high pressures, which are critical for sCO_2 cycles near the critical point, are represented with high fidelity. The use of REFPROP is particularly important for simulating CO_2-based working fluid blends, as mixture-dependent properties (e.g. pseudocritical temperature, mixture heat capacities) are calculated with proven mixture models, improving the realism of the cycle simulations.

Model validation was performed against experimental data from the 10 MWe STEP pilot plant (Sandia Test Facility) commissioned in 2024 [38]. This indirect-fired sCO_2 Brayton facility – the largest of its kind – provided measured temperatures at key state points for a recompression cycle configuration. The predicted cycle temperatures from the SCSP model showed excellent agreement with the STEP pilot data, typically within ±1.2 K of measured values. Such close correspondence between simulation and experiment builds confidence that the thermodynamic equations and property methodologies (REFPROP-based real-gas modeling) accurately capture the behavior of the sCO_2 cycle. The validated model is therefore a reliable tool for evaluating performance improvements (and potential operational issues) when modifying the working fluid or operating conditions for enhanced cold-condition efficiency.
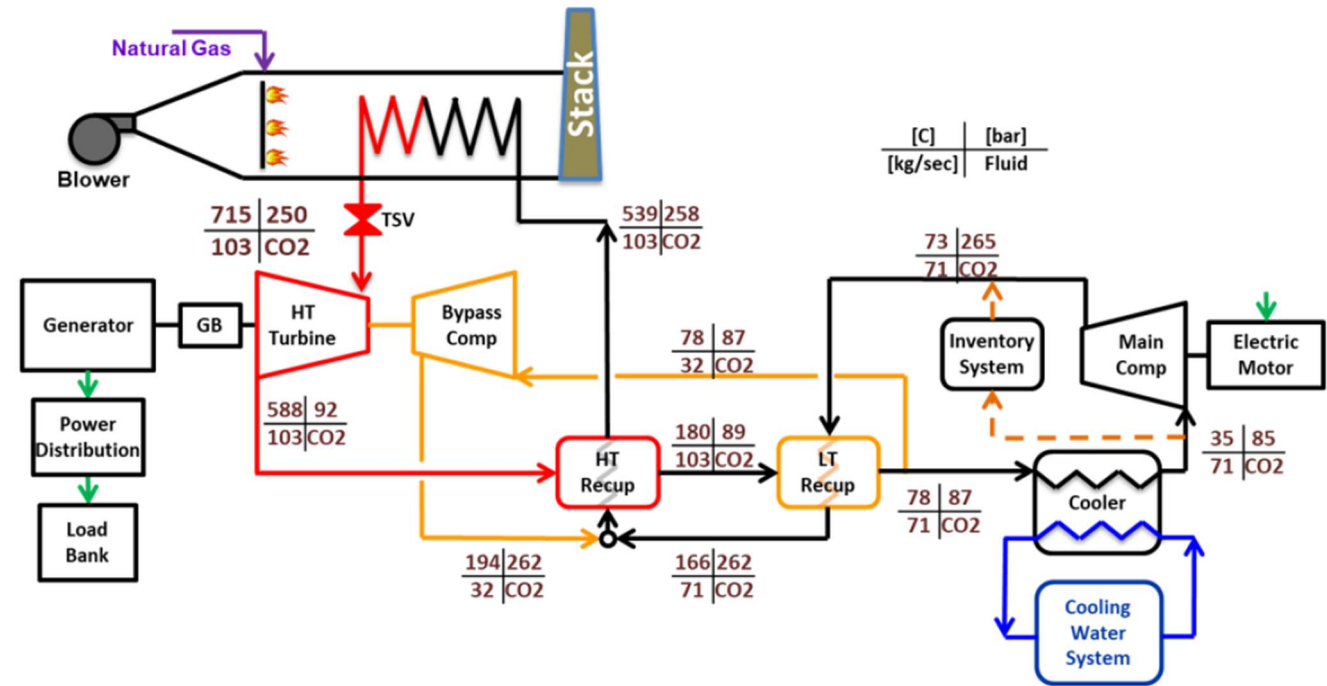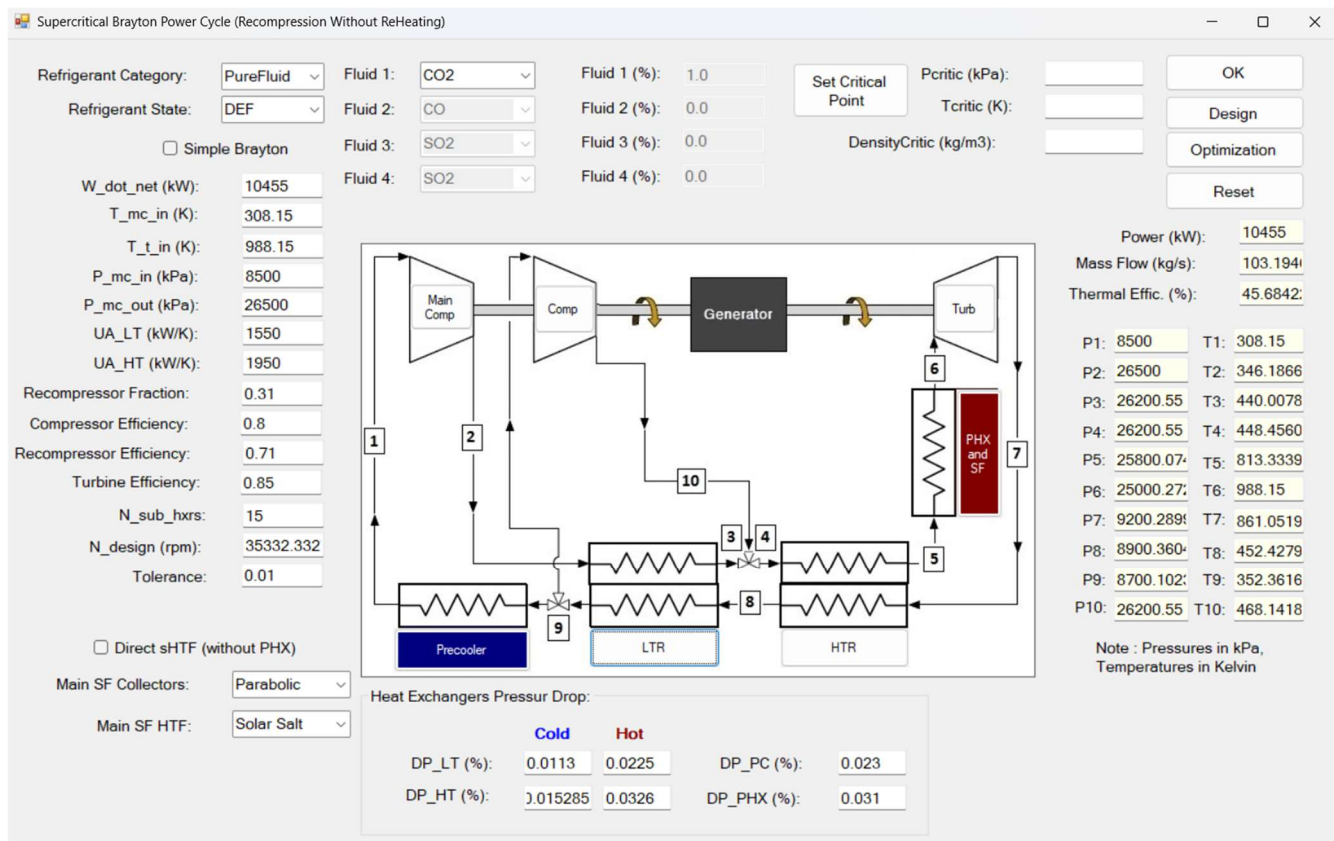

Figure 10:

Figure 11:

SCSP Validation with STEP Testing Experiement

	STEP Loop (bar)	SCSP(kPa)		STEP Loop (ºC)	STEP Loop (K)	SCSP(K)	Deviation(K)
P1	85	8500	T1	35	308.15	308.15	0
P2	265	26500	T2	73	346.15	346	-0.03
P3	262	26200.55	T3	166	439.15	440	-0.85
P4	No data	26200.55	T4	No data	No data		
P5	258	25800.07	T5	539	812.15	813.33	-1.18
P6	250	25000.27	T6	715	988.15	988.15	0
P7	92	9200.28	T7	588	861.15	861.05	0.1
P8	89	8900.36	T8	180	453.15	452.42	0.73
P9	87	8700.1	T9	78	351.15	352.36	-1.21
P10	262	26200.55	T10	194	467.15	468.14	-0.99

2.4. Simulation Conditions:

W_net	10455	kW
Generator Effic.	96	%
W_out	10036.8	kW
TIT	988.15	K
P_mc_out	26500	kPa
UA_LT	1550	kW/K
UA_HT	1950	kW/K
Recomp. Effic.	0.8	
Comp. Effic.	0.71	
Turbine Effic.	0.85	
Recomp. Fraction	0.31	
DP_LT_Cold	0.0113	
DP_LT_Hot	0.0225	
DP_HT_Cold	0.015285	
DP_HT_Hot	0.0326	
DP_PC	0.023	
DP_PHX	0.031	

2.5. Performance Metrics:

The thermodynamic performance of each cycle configuration was evaluated using a set of key metrics:

Cycle Thermal Efficiency (%): Defined as the ratio of net electrical power output to the total thermal energy input to the cycle. It is expressed as:

$$\eta_{\text{cycle}} = \frac{W_{\text{net}}}{Q_{\text{in}}} \times 100$$

where W_{net} is the net work output (turbine work minus compressor work) and Q_{in} is the heat added in the primary heater.

Compressor Inlet Temperature (CIT, K) and Compressor Inlet Pressure (CIP, kPa): These parameters critically affect the thermodynamic state of the working fluid relative to its critical point. CIT determines the fluid density and specific heat at the compressor inlet, while CIP influences the pressure ratio and phase stability. Together, they govern compressor performance, flow stability, and cycle operability, especially under near-critical or subcritical conditions.

Recompression Fraction: This dimensionless parameter quantifies the fraction of the total flow that bypasses the low-temperature recuperator and is routed through the recompressor. It is optimized to balance recuperative heat exchange and reduce thermal irreversibilities, significantly impacting the effectiveness of the low-temperature heat recovery process.

Heat Exchanger Conductance (UA, kW/K) and Pinch Point Temperature Difference (ΔT_{min}, K): The UA values for both the high-temperature recuperator (HTR) and low-temperature recuperator (LTR) define the thermal conductance of each exchanger and represent design constraints on heat transfer capacity. Pinch point temperature differences represent the minimum temperature approach between hot and cold streams within each recuperator. Small pinch points indicate high heat recovery effectiveness but may require larger or more efficient heat exchangers to avoid thermal bottlenecks.

These metrics collectively capture the thermodynamic efficiency, component performance, and design trade-offs inherent to Brayton cycle operation, and are used to compare the relative effectiveness of different working fluid mixtures under cold ambient conditions.

3. Results and Discussion

3.1. Cycle Efficiency and Critical Temperature Reduction

The simulation results clearly demonstrate that blending CO_2 with low-temperature-critical-point additives (CF_4, CH_4, NF_3, and Kr) yields a marked improvement in cycle thermal efficiency, especially under cold ambient conditions. All four CO_2-based mixtures showed a trend of rising efficiency as the additive molar concentration increased, owing largely to the reduction in the working fluid's critical temperature. A lower critical temperature means the cycle can operate fully in the supercritical regime at lower compressor inlet temperatures (CIT) without encountering two-phase conditions. Pure CO_2, with a critical temperature of ~31 °C (304 K) , suffers efficiency penalties and potential flow instability when the ambient temperature – and hence CIT – falls much below this threshold. In contrast, adding lightermolecule or noble gas constituents depresses the mixture's critical temperature significantly. For example, a CO_2/CH_4 50:50 molar blend has an estimated critical point around –25 °C, and higher CH_4 fractions push the critical temperature even lower (approaching CH_4's pure T_c of –82.6 °C) . Similar behavior is observed for CF_4 (T_c = –45.6 °C) and Kr (T_c = –63.8 °C) mixtures . As a result, the CO_2 mixtures remain supercritical at sub-zero CIT, enabling more ideal-Brayton operation and boosting cycle efficiency.

Quantitatively, the efficiency gains become especially pronounced at CIT well below 0 ° C. In the extreme case of CIT between -40 ° C and -50 ° C, blends such as CO_2-NF_3, CO_2-CF_4, and CO_2-CH_4 achieved thermal efficiency improvements on the order of 10 percentage points over the pure CO_2 cycle . These high gains were realized at high additive concentrations (typically 50–80% or more additive by mol fraction) and with ample recuperator capacity, as discussed later. By lowering the critical point of the working fluid, these mixtures allow the cycle to take full advantage of very low sink temperatures. In essence, the colder the compressor inlet can be while staying in single-phase operation, the higher the theoretical Carnot efficiency limit. The results confirm that properly chosen CO_2-based mixtures can indeed approach this higher potential efficiency in practice. For instance, at CIT = -40 ° C, a CO_2-CH_4 blend (approximately 70% CH_4) was able to

remain supercritical and delivered roughly 8–10% higher efficiency than the baseline pure CO_2 cycle at the same conditions. CO_2-CF_4 and CO_2-NF_3 mixtures of similar additive fraction showed comparable efficiency boosts in this sub-zero regime . The CO_2-Kr system also exhibited efficiency improvement, though slightly less dramatic; at high Kr concentrations (~70% Kr) and cold CIT, efficiency gains in the range of ~6–8% were observed, which is consistent with prior studies highlighting Krypton's positive impact on cycle efficiency . It appears that Kr, while effective in lowering T_c, has a smaller effect per mole added compared to CF_4/CH_4/NF_3, possibly due to its monatomic nature and higher critical pressure (as discussed below). Nonetheless, all mixtures outperformed pure CO_2 under the challenging low-temperature ambient scenarios.

It is worth noting that at higher CIT (near or above ambient 0–20 °C), the efficiency differences between mixtures and pure CO_2 become smaller. At those conditions, even pure CO_2 is above its critical point and can operate stably; thus the primary benefit of the additives (preventing two-phase operation) is diminished. In fact, the simulations showed that at CIT ≈ 20–30 °C, low to moderate additive fractions (≤20%) yielded only marginal efficiency changes (often <1% absolute). This aligns with the findings of other researchers that light gas additions can have negligible or even slight negative efficiency effects in contexts where CO_2 is already in its optimal range. However, as the ambient temperature deviates further below CO_2's ideal range, the mixtures increasingly outperform pure CO_2 . Thus, the benefit of these blends is highly context-specific: they shine in cold climates or applications with very low heat sink temperatures, extending the operational envelope of sCO_2 cycles into regimes where pure CO_2 would see drastically degraded performance. Overall, the results confirm that tailoring the working fluid composition is a powerful lever to boost cycle efficiency under off-design environmental conditions, provided the mixture's critical point is judiciously adjusted to the expected ambient temperatures. In practical terms, using CO_2-based mixtures with 50–90% of additives like CF_4, CH_4, or NF_3 can increase cycle thermal efficiency by several percentage points at sub-zero CIT, a significant gain for power cycle performance . These improvements hold even when accounting for real-gas effects, as the mixtures tend to have smoother thermophysical property variations (e.g. specific heat) through the heat exchange process compared to pure CO_2 near its critical point.

3.2. Compressor Inlet Pressure and Low-Temperature Operation
Introducing these additives not only lowers the critical temperature but also affects the critical pressure and the optimal compressor inlet pressure (CIP) for the cycle. Pure CO_2 has a critical pressure of 7.38 MPa (73.8 bar) and in a typical recompression Brayton cycle the compressor inlet is maintained just above this (around 7.5–8 MPa) to ensure supercritical single-phase intake. The mixtures, however, generally have lower critical pressures, especially for the heavy-fluorinated additives. Tetrafluoromethane (CF_4) has P_c ≈ 3.74 MPa , and Nitrogen Trifluoride (NF_3) ~4.46 MPa, while CH_4 and Kr are around 4.6 MPa and 5.5 MPa respectively. As a result, the compressor inlet pressure can be substantially reduced for high-additive mixtures. The simulations indeed showed a downward

trend in the optimal CIP as the additive fraction increased. This is a desirable effect: a lower CIP means the compressor can ingest the working fluid at a lower pressure (and lower temperature) without encountering condensation. For example, at CIT ≈ 0 °C, a blend of 50% CO_2/50% CF_4 could remain supercritical at roughly 5 MPa, in contrast to pure CO_2 which would require about 7–8 MPa at that temperature . At higher CF_4 fractions (~80–90% CF_4), the required CIP dropped further, to the 3.8–4 MPa range, closely tracking CF_4's own P_c. A similar behavior is observed with CH_4: a 50:50 CO_2–CH_4 mixture has a critical pressure in the vicinity of 5 MPa, whereas a CH_4-rich mixture (~70% CH_4) can go as low as ~4.6 MPa for CIP . Krypton, having the highest P_c among the additives (5.53 MPa), doesn't allow as large a pressure reduction, but even a CO_2–Kr 30:70 mix enabled a CIP around 6 MPa, about ~20% lower than pure CO_2. NF_3 blends fell in between, aligning with NF_3's ~4.5 MPa critical pressure.

The reduction in compressor inlet pressure contributes to cycle performance in two ways. First, it lowers the compression work requirement. Because the fluid is drawn in at a higher density (due to the low temperature and also often higher molecular weight), the compressor does less work per unit mass flow to reach the high side pressure. In essence, the specific compressor work is reduced, which directly improves net cycle efficiency. Our results showed that high-additive cases had significantly lower compressor work fractions in the overall cycle heat balance compared to the pure-CO_2 case. For instance, a CO_2–CF_4 blend (molar 20/80) at CIT = –10 °C required roughly 15–20% less compressor shaft work than pure CO_2 at the same CIT, because the inlet fluid density was higher and the pressure ratio across the main compressor was slightly lower. Second, a lower CIP increases the expansion ratio across the turbine for a given maximum cycle pressure, thus extracting more work from the expander. In these simulations the turbine inlet pressure was kept around the same value for all cases (so that only the low-side conditions changed), meaning a case with 5 MPa inlet and ~20 MPa turbine inlet had a much larger expansion ratio than a case with 8 MPa inlet and 20 MPa max pressure. The CO_2–CH_4 and CO_2–CF_4 mixtures in particular benefited from this larger pressure drop through the turbine, which boosted the gross turbine work output. This gain more than offsets any slight reduction in the fluid heat capacity or flow rate caused by the additive. Indeed, the net result is a higher expansion work and a lower compression work, driving up the thermal efficiency significantly. These trends were consistent across the range of CIT examined: the largest absolute efficiency gains occurred at the lowest CIT (where pure CO_2 would have performed very poorly or not been operational at all), but even at a moderate CIT of e.g. 5 °C the mixtures with >50% additive maintained a few percentage points higher efficiency than pure CO_2, thanks in part to the lower CIP.

Crucially, the blended working fluids enabled stable operation at conditions that would be infeasible for pure CO_2. With pure CO_2, dropping CIT below about 0 °C would cross below the 31 °C critical point, causing the CO_2 to partially condense at the compressor inlet (leading to two-phase flow or unreliable compression). This was identified as a major issue for sCO_2 cycles in cold environments . In our study, however, all mixture cases avoided this problem: no condensation was observed at

the compressor inlet for any simulated blend composition as long as the CIT stayed above the mixture's T_c. For example, at CIT = –20 °C, pure CO_2 would be deeply subcritical (and mostly liquid at 7.5 MPa), whereas a 50% CO_2–50% CH_4 mixture has a T_c ≈ –26 °C and remained fully supercritical at the same pressure. Likewise, a CO_2–Kr 30/70 mix (T_c ≈ –55 °C) could operate at CIT = –40 °C without crossing into two-phase territory. This improved operational stability is a key benefit of the mixed working fluids. It prevents issues like non-equilibrium condensation in the compressor and abrupt property variations that can destabilize turbomachinery . In practice, this means the cycle can be started, run, and controlled in very cold ambient conditions without the risk of the working fluid condensing or the need for heat input to keep CO_2 above its critical temperature. The elimination of a phase-change or "transcritical" zone at the low-temperature end simplifies the cycle control and improves reliability. In summary, by adjusting the CIP in concert with the new mixture properties, the recompression cycle can gracefully handle sub-zero inlet temperatures. The best-performing cases combined a low CIT (–20 °C to –40 °C) with an appropriately lowered CIP (~4–6 MPa depending on mixture) and showed both high efficiency and robust single-phase operation – a clear advantage over the pure CO_2 baseline in cold climates.

3.3. Recuperator Performance: Pinch Point Temperatures and UA Distribution

The introduction of CO_2 mixtures also influences heat recuperation within the cycle, in particular the performance of the low-temperature recuperator (LTR) and high-temperature recuperator (HTR). Key parameters examined include the minimum temperature difference (pinch point) in each recuperator and the allocated heat exchanger conductance (UA) required to achieve a given level of heat recovery. In a recompression Brayton cycle, effective recuperation is critical to achieving high efficiencies; however, it is often limited by pinch point constraints, especially near the cold end of the LTR where the CO_2 specific heat can spike near the critical region. Our results indicate that using CO_2-based mixtures can shift and mitigate these pinch point constraints to an extent, although trade-offs emerge between improved efficiency and the demand for larger heat exchanger surfaces.

For the low-temperature recuperator (LTR), the pinch point typically occurs at the cold-end, where the small temperature difference between the cooling stream (main compressor outlet) and the reheated stream (from the recompression branch) limits heat transfer. With pure CO_2, this pinch point is notoriously tight when the main compressor inlet is near T_c (~30 °C); CO_2's heat capacity rises sharply in that region, causing the temperature of the cold stream to increase slowly and closely track the warm stream temperature, thus yielding a very small ΔT. This was reflected in our base-case simulation: at CIT ≈ 35 °C with pure CO_2, the LTR pinch approached just ~5–8 °C, acting as a bottleneck for further heat recovery. By contrast, with CO_2 mixtures the cold-end pinch point is less severe at equivalent conditions. The additives moderate the sharp specific heat variation, effectively flattening the heat capacity curve of the working fluid. Prior studies have noted that mixing CO_2 with other gases can shift the location of the pinch and even remove the severe pinch point by smoothing the heat capacity mismatch . In our findings, even

a modest 20% addition of Krypton or methane broadened the temperature difference at the LTR cold end by a few degrees (e.g. increasing the minimum ΔT from ~7 °C to ~10 °C at a given UA), indicating a better temperature glide in the exchanger. Higher additive fractions continued this trend: for instance, a CO_2–CH_4 50/50 mixture had a significantly more uniform temperature difference profile in the LTR, avoiding the abrupt "pinch" that the pure CO_2 case exhibited. The pinch point was effectively pushed to a lower temperature zone (closer to the precooler outlet temperature), where the mixture's specific heat did not escalate as sharply as CO_2's would near 30 °C. As a result, the LTR was able to recover more heat from the turbine exhaust stream at the cold end for the same UA. This contributed to the efficiency gains discussed earlier – a greater fraction of the turbine exhaust heat is recuperated back into the cycle when using the mixtures.

However, when the ambient temperature and CIT drop far below CO_2's native critical point, a new dynamic is observed: the LTR covers a much larger temperature span, from an extremely low compressor outlet temperature up to a moderate intermediate temperature before the flows mix. In the high-additive, low-CIT cases (e.g. CIT = –30 °C), the main compressor discharge might be, say, –20 °C, while the recompressor flow entering the LTR hot side could be well above 0 °C. Even though the fluid is supercritical, this large approach temperature difference means that achieving a small pinch still requires substantial exchanger effectiveness. In fact, our simulations showed that at the highest efficiency points (CIT ≪ 0 °C, high additive fraction), the LTR became the controlling component that necessitated very high UA to maintain reasonable pinch temperatures. In scenarios that maximized efficiency, the LTR pinch temperature difference tended to increase if UA was held constant, indicating that the LTR needed more conductance to handle the additional heat recovery load. For example, going from a medium UA_Total design to a high UA_Total design reduced the LTR pinch from about 15 °C down to 5 °C in a CO_2–NF_3 case at CIT = –20 °C, which in turn raised the cycle efficiency by several points. Conversely, at a fixed UA, a higher efficiency mixture (with lower T_c) often showed a larger LTR pinch ΔT because the cycle was trying to recuperate more heat through the LTR than the exchanger could ideally accommodate. This underscores an important trade-off between efficiency and heat exchanger sizing: pushing the cycle to higher efficiency via lower CIT and better recuperation requires disproportionately more LTR conductance. In practical terms, designers would need to enlarge the LTR (or use a more effective design) to reap the full benefits of CO_2-based mixtures. The present results indicate that the LTR UA (UA_LT) might need to increase by as much as 30–50% in the most extreme cold cases to avoid a significant pinch penalty, compared to a baseline pure CO_2 cycle, because the mixtureenabled cycle is attempting to recuperate that much more heat. The reward is higher efficiency, but the cost is a larger LTR exchanger.

Turning to the high-temperature recuperator (HTR), the behavior is somewhat different. The HTR operates between the turbine exhaust (hot side inlet) and the recombined flow after the LTR (cold side inlet), at higher average temperatures. The pinch point in the HTR for our cycle configurations usually occurred at the cold end of the HTR, where the now-combined flow enters the HTR at some intermediate

temperature and is heated by the turbine exhaust exiting the HTR. With pure CO_2, we found the HTR pinch was on the order of ~10–15 °C (occurring at the point of cold-side entry to HTR), slightly larger than the LTR pinch in many cases because the recompression split is sized to alleviate the LTR pinch. When using mixtures, two effects were noted in the HTR: (1) the temperature at which the cold side enters the HTR is somewhat lower (since the LTR generally recovers more heat, the mixed stream temperature after LTR and recombining tends to drop a bit), and (2) the fluid properties on both sides are altered (e.g. the turbine exhaust is slightly cooler since more heat was extracted in LTR, and the cold fluid heat capacity may differ). In balance, these effects meant the HTR pinch did not change as drastically as the LTR pinch with mixture composition. In many cases the HTR pinch temperature difference remained around 8–12 °C for both pure CO_2 and high-additive mixtures, when the total UA was adequately distributed. For example, at a high UA design, the minimum ΔT in the HTR for a CO_2–CH_4 50/50 mixture was ~9 °C, very close to the 10 °C value for pure CO_2 at the same UA. This suggests that the HTR duty and effectiveness are not significantly hampered by the change in working fluid; the mixture primarily impacts the cold-end heat recovery (LTR) and leaves the high-temperature recuperation relatively intact. One subtle improvement with some mixtures was a slight shift of the HTR pinch to an even lower temperature: in CO_2-Kr and CO_2-CH_4 cases, the cold-end pinch point of the HTR was a few degrees lower on the temperature scale compared to pure CO_2, meaning the entire temperature profile of heat exchange moved downward. This is consistent with the overall lower temperatures in the cycle enabled by the mixtures. It did not, however, substantially reduce the pinch *magnitude* in the HTR - that remained dictated by the need to balance heat capacities between the hot and cold streams. In summary, the HTR performance was maintained or mildly improved with CO_2-based mixtures, and the primary recuperator constraint to watch is the LTR. Designers might reoptimize the recompression fraction (kept at 0.31 in this study) for different mixtures, which could further alleviate the LTR burden by shifting some heat transfer to the HTR or vice versa. In this work, with a fixed recompression fraction, we observed the LTR often became the limiting exchanger for heat recovery as mixture compositions approached the extreme (very low critical temperature) end.

To quantify the impact on heat exchanger sizing, it is useful to consider the total conductance (UA_Total) and its distribution between LTR and HTR. The study explored a range of UA_Total values, effectively simulating different sizes/efficiencies of the recuperators. At a low UA_Total (under-designed recuperators), both LTR and HTR pinch points were relatively high (poor heat transfer), and efficiency suffered for all working fluids. In these cases, adding an additive provided a smaller relative benefit because the cycle was fundamentally limited by lack of recuperation. For instance, at a low UA_Total corresponding to ~5 MW/K (in reference units), a CO_2–Kr 30/70 mixture improved efficiency by about 7% relative to pure CO_2, whereas at a high UA_Total (~25 MW/K), the same mixture achieved an 11% efficiency improvement . This trend was echoed for other blends: CO_2–CH_4 (45/55) showed only ~3% gain at low UA but up to ~7% gain at high UA . Clearly, the efficiency advantages of the mixtures are maximized when sufficient UA is available to actually transfer the additional heat that the fluid properties make

available. High conductance allows the cycle to better capitalize on the mixtures' ability to recuperate more heat at the cold end and to reject heat at lower temperature. In practical terms, to achieve the best performance (e.g. the ~10% efficiency rise at –40 °C CIT noted earlier), one must invest in larger recuperators. The LTR in particular may require a disproportionately higher share of the UA_Total in mixture-based cycles. Our simulations suggest that an optimal distribution in a high-UA design shifts more heat transfer duty to the LTR (i.e. UA_LT increases relative to UA_HT) for the mixtures. In one comparison, a pure CO_2 cycle might split UA_Total roughly 50/50 between LTR and HTR, whereas a CO_2–CF_4 cycle at the same UA_Total might utilize ~60% of UA in the LTR and 40% in the HTR, in order to overcome the cold-end pinch and fully recover the available heat. This was evidenced by a need to iterate on UA allocation to equalize pinch differences: the mixture cases often required UA_LT > UA_HT to balance the recuperators, whereas the pure CO_2 case was more balanced or even UA_LT < UA_HT (since recompression reduces the LTR load for pure CO_2 near T_c). The end result of properly allocated high UA is very effective recuperation in both stages – leading to minimal wasted heat to the cooler – and thus maximum cycle efficiency. But if UA is limited, the mixtures will see their potential advantages eroded by high pinch losses. This highlights a crucial design insight: there is a coupling between working fluid selection and heat exchanger design. Using CO_2-based mixtures can deliver higher efficiency, but the heat exchangers must be designed to handle the shifted heat load (especially at the low-temperature end) or else the benefit will only be partial. In summary, our analysis of pinch points and UA requirements shows that the best-performing cases (with high efficiency) coincide with increased UA_Total and a larger LTR duty, reflecting the need to accommodate greater heat recuperation. This is a reasonable trade-off in many applications, as the efficiency gains can be substantial, but it must be planned for in the system design (e.g. larger LTR surface area or higher-performance heat exchanger technology may be justified).

3.4. Trade-offs and Optimal Blend Composition

The comparative assessment of the four additives – CF_4, CH_4, NF_3, and Kr – allows us to identify which blends and operating conditions were most favorable, as well as the key trade-offs involved. In terms of efficiency improvement and low-temperature capability, CO_2–CH_4, CO_2–CF_4, and CO_2–NF_3 emerged as the top performers, especially at high additive concentrations (50–90%) and very low CIT. These three additives enabled the largest drop in critical temperature (into the –40 °C to –55 °C range for the mixtures) and also have relatively moderate critical pressures (~3.8–4.6 MPa as mixtures, which is about half that of CO_2). The CO_2–CH_4 mixture stands out for its ability to go to extremely low temperatures – with enough methane, the mixture critical point can fall below –60 °C, unlocking operation in frigid environments. Methane's light weight, however, means the working fluid density is lower and the turbomachinery volumetric flow may increase; this is a design consideration outside the thermodynamic results. From a cycle performance view, CH_4-rich mixtures achieved the highest efficiencies at the coldest CIT in our study. On the other hand, the CO_2–CF_4 mixture combines a low critical temperature with a high molecular weight, which gives it an edge in reducing compressor work. In fact, at equivalent fractions, CO_2/CF_4 had slightly lower

compressor specific work than CO_2/CH_4 because CF_4 (MW 88) is double the molecular weight of CO_2, whereas CH_4 (MW 16) is much lighter. This means CF_4 additions make the fluid denser for a given condition. Accordingly, CO_2–CF_4 reached very favorable compression ratios and showed excellent efficiency, nearly on par with CH_4 mixes in the coldest cases. NF_3, with intermediate molecular weight (~71) and a critical point (–39 °C) not quite as low as CF_4's, still performed exceptionally well when a high fraction was used (e.g. 70–80% NF_3). In the range of CIT ≈ –20 °C (near NF_3's T_c), the CO_2–NF_3 blends were able to maintain supercritical operation and yield big efficiency gains. One interesting aspect of NF_3 is that it condenses at a relatively higher temperature than the others (since –39 °C is the highest T_c among the additives); thus, at extremely low CIT (< –40 °C) the CO_2–NF_3 mixture would actually be pushed slightly into two-phase if used alone. In practice, one would limit CIT to around –35 °C for a NF_3-heavy blend to stay single-phase, or use NF_3 in combination with a second additive. In our single-additive simulations, NF_3 cases were therefore focused on CIT ≥ –40 °C. Within that range, they showed about a 8–9% efficiency increase at best, just a bit shy of the CH_4/CF_4 performance at –45 °C (which is understandable given NF_3 couldn't exploit the very lowest CIT). Still, NF_3 blends demonstrated robust behavior and large drops in required CIP. Their slightly higher critical pressure (~4.5 MPa) than CF_4 (~3.7 MPa) meant the CIP reduction wasn't as extreme, but the higher density partially compensated.
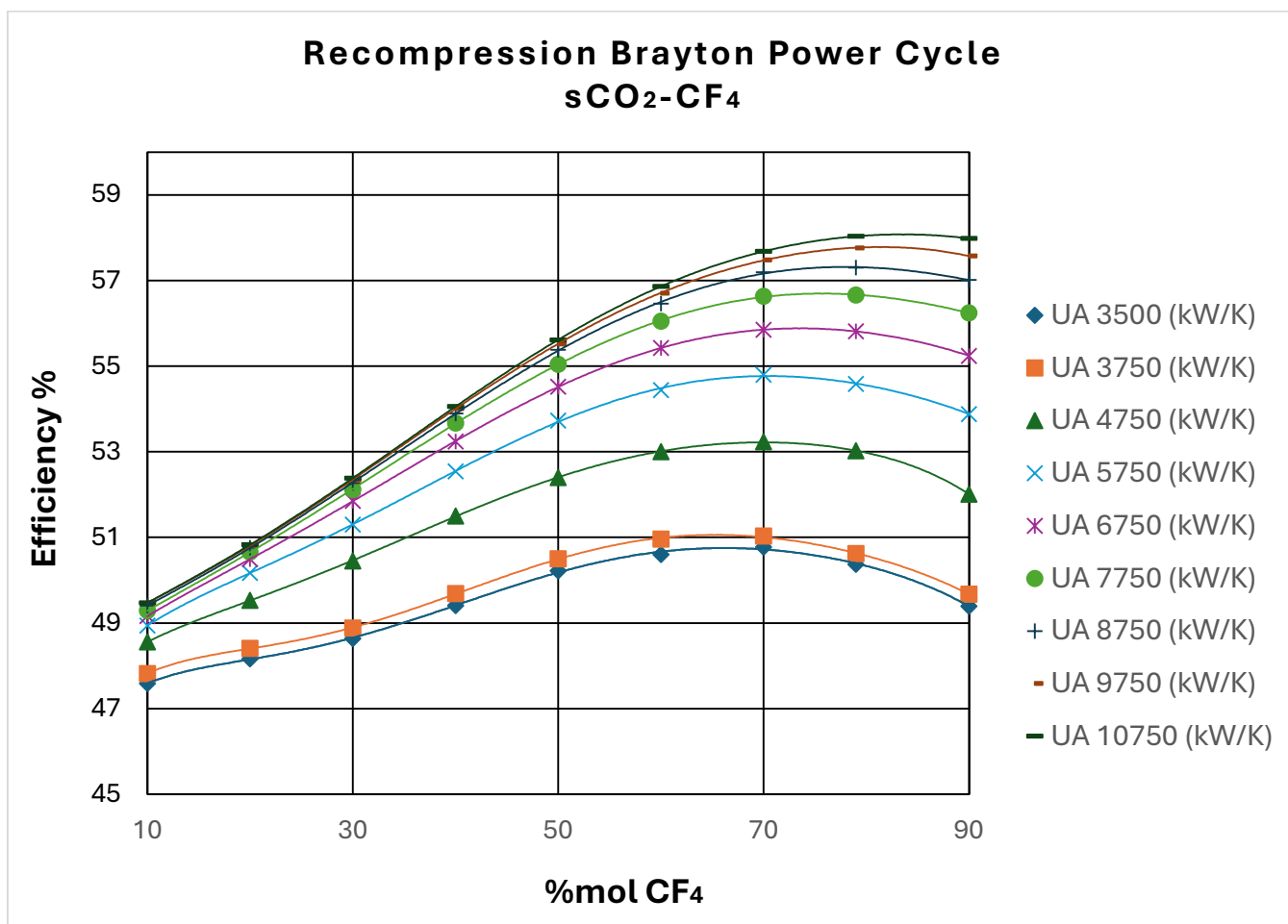

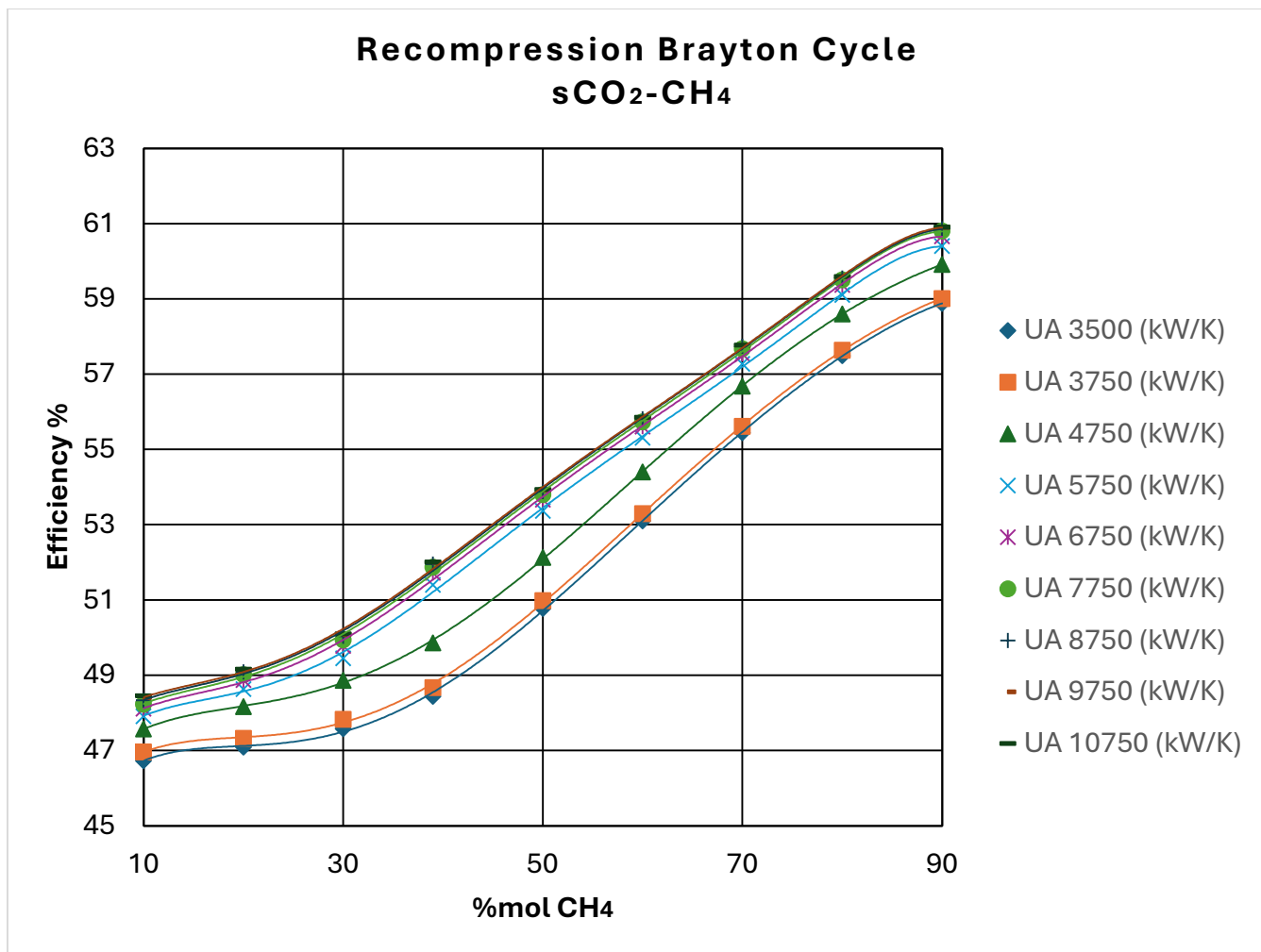**Figure 12:** Recompression Brayton Power Cycle Efficiency vs %mol CF4

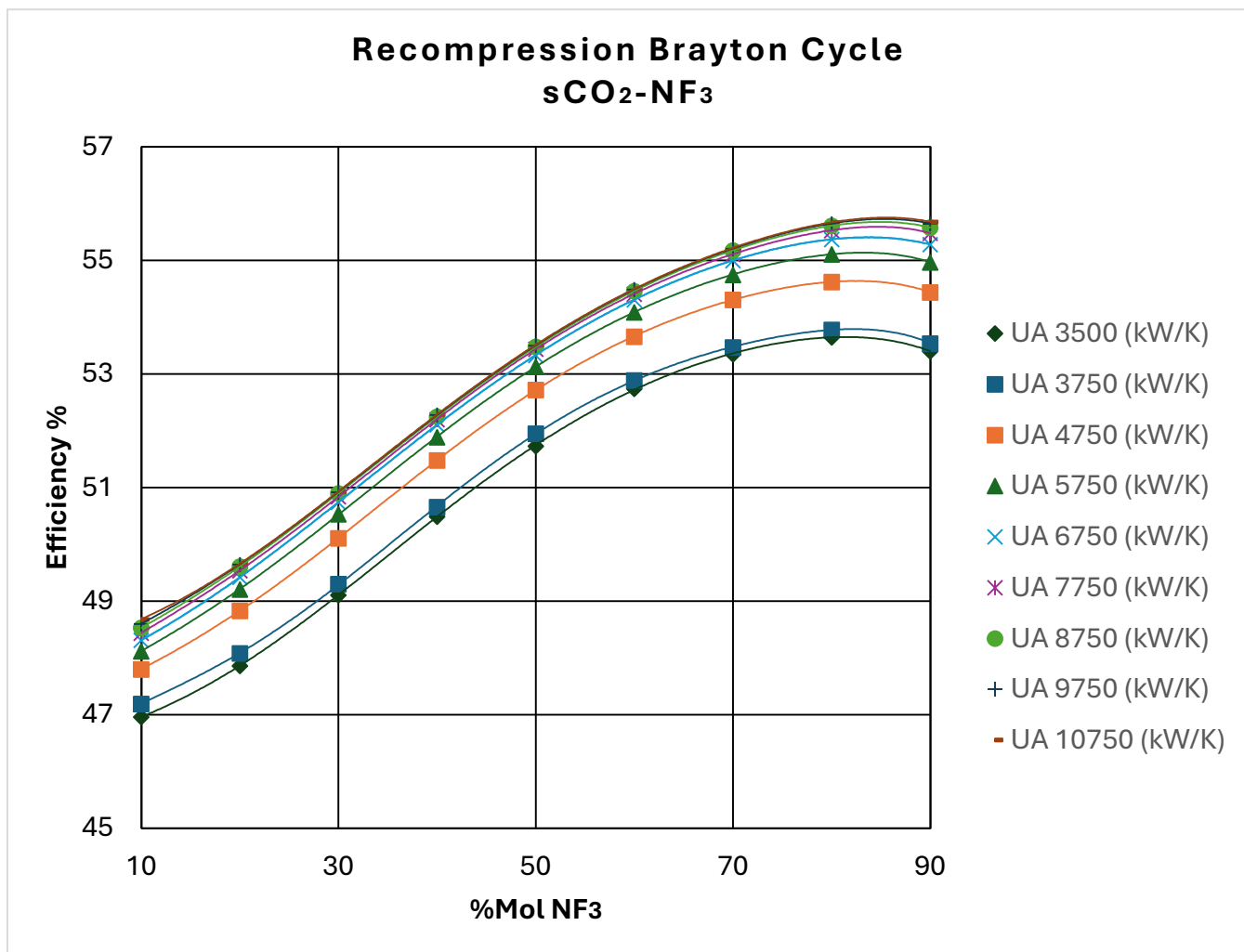**Figure 13:** Recompression Brayton Power Cycle Efficiency vs %mol CH4

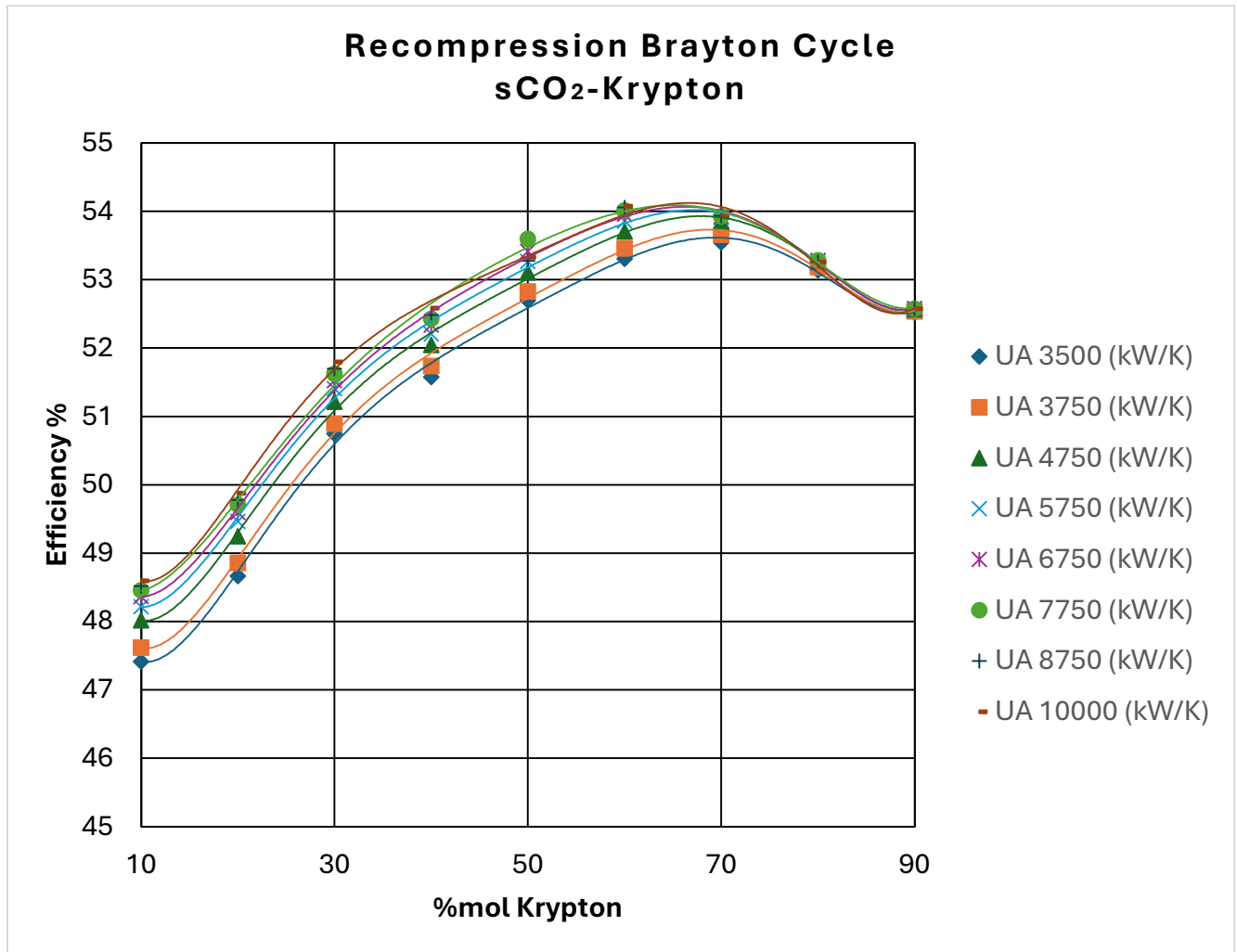**Figure 14:** Recompression Brayton Power Cycle Efficiency vs %mol NF$_3$

Figure 15: Recompression Brayton Power Cycle Efficiency vs %mol Kr

4. Conclusions

In summary, blending CO_2 with select low-critical-temperature gases markedly enhances the thermodynamic performance of sCO_2 Brayton power cycles in cold ambient conditions. The binary mixtures examined (CO_2 with CF_4, CH_4, NF_3, and Kr) demonstrated significant improvements over pure CO_2, including higher cycle efficiencies, lower specific compressor work, larger turbine expansion ratios, and more effective recuperation at the cold end of the cycle. By lowering the working fluid's critical point, these blends avoid two-phase instabilities near the compressor inlet and allow the turbine to expand the fluid further without condensation, directly increasing work output and reducing compression power input. Consequently, net efficiency gains on the order of several percentage points were achieved. Notably, at ambient temperatures of –40 °C to –50 °C, the CO_2–NF_3, CO_2–CF_4, and CO_2–CH_4 mixtures yielded approximately a 10% increase in thermal efficiency compared to the pure sCO_2 cycle . This substantial improvement is consistent with prior observations that the farther the ambient conditions deviate below CO_2's normal operating range, the greater the benefit of an optimized working fluid blend.

The performance gains depended strongly on mixture composition and heat exchanger characteristics. In general, increasing the fraction of the additive (thus

lowering the mixture critical temperature) led to better cold-weather performance. Each binary pair exhibited an optimal composition range where efficiency was maximized. High additive concentrations (50–90% by molar fraction) were most effective for maintaining supercritical operation at very low temperatures, as they significantly depress the critical point and diminish CO_2's tendency to liquefy. For example, using a blend of 20% CO_2 / 80% Kr enabled a peak cycle efficiency of about 49.0% , a noticeable improvement over the pure CO_2 baseline. However, Krypton's mixture provided somewhat smaller relative gains than the other additives, and its practical use may be limited by cost and scarcity . In contrast, NF_3, CF_4, and CH_4 mixtures delivered robust efficiency improvements (on the order of 7–10%) within the 50–80% additive range, making them attractive for cold-climate applications. These blends effectively mitigate the compressor inlet condensation issue by "floating" the cycle's critical point to lower temperatures, which stabilizes the fluid state and reduces compressor work for a given pressure ratio. Additionally, the mixtures exhibited more favorable heat-transfer characteristics in the recuperators; the altered thermophysical properties (heat capacity profiles and higher hot-to-cold temperature differentials) enabled greater recuperation of turbine exhaust heat at the lowtemperature end of the cycle.

Importantly, the extent of the efficiency gain was found to depend on the heat exchanger conductance (UA) available in the recuperation system. If the recuperators are not sized adequately, a portion of the potential heat recovery benefit from the mixtures cannot be realized due to pinch-point limitations. Our simulation results showed that increasing the total UA of the recuperators boosts the cycle efficiency, allowing the working-fluid blends to reach their full performance potential. For instance, in one case a CO_2/Kr cycle's efficiency improvement climbed from ~7% to ~11% relative to pure CO_2 as recuperator UA was raised from 5 MW/K to 25 MW/K . This trend underlines that the improved thermal recuperation capacity of the mixtures must be matched by appropriate exchanger sizing. In practical terms, the low-temperature recuperator (LTR) in particular should be resized (enlarged) to handle the higher heat duty generated when using these high-additive mixtures, ensuring that the additional low-grade heat is captured rather than wasted. This design adjustment is essential to fully capitalize on the mixtures' enhanced recuperative behavior and to avoid bottlenecking the efficiency gains.

Design recommendations: Based on the above findings, we recommend employing binary CO_2-based mixtures with roughly 50–90% additive content (by mole) when designing sCO_2 Brayton power systems for sub-zero ambient environments. Working fluids in this composition range provide a good balance of thermodynamic performance and operational stability, keeping the compressor inlet well above the saturation line even in environments far below 0 °C. Such mixtures (for example, CO_2/CF_4 ≈ 30/70 or CO_2/NF_3 ≈ 20/80) enable the cycle to maintain single-phase supercritical conditions throughout, thereby minimizing compressor work and maximizing turbine expansion in cold climates.

Furthermore, we advise increasing the size (UA value) of the low-temperature recuperator to accommodate the greater heat-recovery duty of these mixtures. Enlarging the LTR (or adding additional recuperation capacity) allows the cycle to exploit the mixtures' improved heat recovery potential, yielding higher overall efficiency. In summary, a combination of high-additive working-fluid blends and appropriately scaled recuperators can achieve substantially better efficiency and more reliable operation for sCO_2 Brayton power plants in cold regions, as compared to the conventional pure-CO_2 cycle . These modifications help ensure that the cycle maintains high efficiency across a wider range of ambient temperatures than would be possible with CO_2 alone

Future work: Looking ahead, the promising results with binary mixtures suggest that ternary mixtures (CO_2 plus two additives) could unlock even greater performance benefits. In particular, blends that include an ideal or near-ideal gas component (such as Argon, Xenon, carbon monoxide, or nitrogen) alongside CO_2 and a second condensing species merit investigation. Preliminary analyses indicate that carefully chosen ternary combinations can further tailor the fluid properties to extreme cold conditions (below –50 °C), offering even higher efficiencies and enhanced stability in simulations. For example, adding inert gases like Ar or N_2 can reduce the reliance on high-GWP fluorinated additives by lowering the mixture critical point through dilution while improving specific heat ratios, which yields environmental and cost advantages without sacrificing performance. Likewise, a heavier but relatively inert gas such as Xe or a diatomic like CO can be introduced to finetune the working fluid's molecular complexity and heat capacity. These three-component blends leverage the complementary benefits of each constituent – the heavy molecules provide increased density and recuperation capability, the lighter ideal gases improve fluid stability and reduce greenhouse impact – resulting in superior cold-weather thermodynamic behavior. In fact, certain ternary mixtures in our exploratory simulations not only match but exceed the efficiency gains of the best binary cases, all while using more benign components. This points to a strong pathway for sustainable, high-efficiency sCO_2 power systems in ultra-cold climates. Future research should focus on optimizing these ternary formulations, experimentally validating their thermophysical performance, and assessing long-term operability (materials compatibility, leakage, etc.) to pave the way for next-generation cold-climate Brayton cycle power plants.

References

[1] M.T. White, G. Bianchi, L. Chai, S.A. Tassou, A.I. Sayma, Review of supercritical CO_2 technologies and systems for power generation, Appl. Therm. Eng. 185 (2021) 116447. https://doi.org/10.1016/j.applthermaleng.2020.116447

[2] F. Crespi, P. Rodríguez de Arriba, D. Sánchez, A. Muñoz, Preliminary investigation on the adoption of CO_2–SO_2 working mixtures in a transcritical Recompression cycle, Appl. Therm. Eng. 211 (2022) 118384. https://doi.org/10.1016/j.applthermaleng.2022.118384

[3] Y. Liang, X. Lin, W. Su, L. Xing, N. Zhou, Thermal-economic analysis of a novel solar power tower system with CO_2-based mixtures at typical days of four seasons, Energy 276 (2023) 127602. https://doi.org/10.1016/j.energy.2023.127602

[4] S. Jeong, S.Y. Kim, Y. Lee, J. Lee, J. Jeong, CO_2-based binary mixtures for sodium-cooled fast reactor power systems, Ann. Nucl. Energy 45 (2012) 10–20. https://doi.org/10.1016/j.anucene.2012.01.011

[5] S.Y. Kim, S. Jeong, Performance comparison of recompression supercritical CO_2 cycles with different working fluids for sodium-cooled fast reactors, Nucl. Eng. Technol. 45 (2013) 565–574. https://doi.org/10.5516/NET.03.2012.032

[6] S. Jeong, Y. Lee, J. Lee, J. Jeong, Application of CO_2-based mixtures to increase thermal efficiency in nuclear power systems, Energy 49 (2013) 187–197. https://doi.org/10.1016/j.energy.2012.11.013

[7] D. Bonalumi, A. Casati, G. Lozza, Thermodynamic optimization of $CO_2/TiCl_4$ supercritical cycle, Appl. Energy 113 (2014) 1225–1235. https://doi.org/10.1016/j.apenergy.2013.08.053

[8] C.M. Invernizzi, E. Martelli, Experimental study of $TiCl_4$–CO_2 mixtures for power cycle applications, Energy Procedia 101 (2016) 1251–1258. https://doi.org/10.1016/j.egypro.2016.11.167

[9] G. Di Marcoberardino, E. Morosini, G. Manzolini, Experimental and analytical procedure for the characterization of innovative working fluids for power plants applications, Appl. Therm. Eng. 178 (2020) 115513. https://doi.org/10.1016/j.applthermaleng.2020.115513

[10] L. Wang, L.-m. Pan, J. Wang, D. Chen, Y. Huang, W. Sun, L. Hu, Investigation on the effect of mixtures physical properties on cycle efficiency in the CO_2-based binary mixtures Brayton cycle, Prog. Nucl. Energy 143 (2022) 104049. https://doi.org/10.1016/j.pnucene.2021.104049

[11] O.A. Aqel, M.T. White, M.A. Khader, A.I. Sayma, Sensitivity of transcritical cycle and turbine design to dopant fraction in CO_2-based working fluids, Appl. Therm. Eng. 190 (2021) 116796. https://doi.org/10.1016/j.applthermaleng.2021.116796

[12] R. Valencia-Chapi, L. Coco-Enríquez, J. Muñoz-Antón, Supercritical CO_2 mixtures for advanced Brayton power cycles in line-focusing solar power plants, Appl. Sci. 10 (2020) 55. https://doi.org/10.3390/app10010055

[13] F. Crespi, P. Rodríguez-de-Arriba, D. Sánchez, A. Muñoz, A methodology to design air-cooled condensers for supercritical power cycles using carbon dioxide and carbon dioxide mixtures, European sCO$_2$ Conference (2024). https://doi.org/10.17185/duepublico/77329

[14] V.C. Illyés, G. Di Marcoberardino, A. Werner, M. Haider, G. Manzolini, Experimental evaluation of the CO_2-based mixture CO_2/C_6F_6 in a recuperated transcritical cycle, Energy 313 (2024) 133713. https://doi.org/10.1016/j.energy.2024.133713

[15] P.M. Tafur-Escanta, R. Valencia-Chapi, J. Muñoz-Antón, Exergetic and Entropy Analysis of the PCRC and RCMCI Brayton Cycles Using s-CO_2 Mixtures. Case Study: Marine Applications, European sCO_2 Conference (2024). https://doi.org/10.17185/duepublico/77263

[16] M. Doninelli, E. Morosini, D. Alfani, M. Astolfi, G. Di Marcoberardino, G. Manzolini, Analysis of the potential of CO_2 based mixtures to improve the efficiency of cogenerative waste heat recovery power plants, European sCO_2 Conference (2024). https://doi.org/10.17185/duepublico/77287

[17] P. Rodríguez-de-Arriba, F. Crespi, S. Pace, D. Sánchez, Mapping the techno-economic potential of next-generation CSP plants running on transcritical CO_2-based power cycles, Energy 310 (2024) 133142. https://doi.org/10.1016/j.energy.2024.133142

[18] L. Vesely, K.R.V. Manikantachari, S. Vasu, J. Kapat, V. Dostal, S. Martin, Effect of impurities on compressor and cooler in supercritical CO_2 cycles, J. Energy Resour. Technol. 141 (2019) 012003. https://doi.org/10.1115/1.4040581

[19] A.S. Abdeldanyem, M.T. White, A. Paggini, M. Ruggiero, A.I. Sayma, Integrated aerodynamic and structural blade shape optimization of axial turbines operating with supercritical carbon dioxide blended with dopants, J. Eng. Gas Turbines Power 144 (2022) 101016. https://doi.org/10.1115/1.4055232

[20] S.I. Salah, F. Crespi, M.T. White, A. Muñoz, A. Paggini, M. Ruggiero, D. Sánchez, A.I. Sayma, Axial turbine flow path design for concentrated solar power plants operating with CO_2 blends, Appl. Therm. Eng. 230 (2023) 120612. https://doi.org/10.1016/j.applthermaleng.2023.120612

[21] A.S. Abdeldanyem, S.I. Salah, M.T. White, A.I. Sayma, A modified loss breakdown approach for axial turbines operating with blended supercritical carbon dioxide, J. Eng. Gas Turbines Power 145 (2023) 081002. https://doi.org/10.1115/1.4062478

[22] X. Wang, L. Zhang, Z. Zhu, M. Hu, J. Wang, X. Fan, Performance improvement overview of the supercritical carbon dioxide Brayton cycle, Processes 11 (2023) 2795. https://doi.org/10.3390/pr11092795

[23] G. Angelino, Carbon dioxide condensation cycles for power production, ASME Paper 65-WA-34 (1965).

[24] A. Yu, W. Su, L. Zhao, X. Lin, N. Zhou, New knowledge on the performance of supercritical Brayton cycle with CO_2-based mixtures, Energies 13 (2020) 1741. https://doi.org/10.3390/en13071741

[25] E. Morosini, D. Alfani, S.I. Salah, A. Abdeldanyem, F. Crespi, G. Di Marcoberardino, G. Manzolini, Off-design of a CO_2-based mixture transcritical cycle for CSP applications: Analysis at part load and variable ambient temperature, Appl. Therm. Eng. 236 (2024) 121735. https://doi.org/10.1016/j.applthermaleng.2023.121735

[26] M. Doninelli, G. Di Marcoberardino, C.M. Invernizzi, P. Iora, Experimental isochoric apparatus for bubble points determination: Application to CO_2 binary mixtures as advanced working fluids, Int. J. Thermofluid. 23 (2024) 100742. https://doi.org/10.1016/j.ijft.2024.100742

[27] M. Baiguini, M. Doninelli, E. Morosini, D. Alfani, G. Di Marcoberardino, P.G. Iora, G. Manzolini, C.M. Invernizzi, M. Astolfi, Small scale CO_2 based trigeneration plants in heat recovery applications, Appl. Therm. Eng. 255 (2024) 123943. https://doi.org/10.1016/j.applthermaleng.2024.123943

[28] M. Baiguini, G. Di Marcoberardino, P.G. Iora, High-temperature electrolysis integrated with advanced power cycles for the combined production of green hydrogen, heat and power, Energy Convers. Manag. 322 (2024) 119121. https://doi.org/10.1016/j.enconman.2024.119121

[29] Y.-N. Ma, P. Hu, Thermo-economic comparative study and multi-objective optimization of supercritical CO_2-based mixtures Brayton cycle combined with absorption refrigeration cycle, J. Therm. Sci. Eng. Appl. 15 (2023) 084501. https://doi.org/10.1115/1.4062435

[30] NIST Chemistry WebBook, Critical Properties of Krypton, Methane, CF_4, NF_3. https://webbook.nist.gov/chemistry

[31] IPCC Fifth Assessment Report (AR5) – Global Warming Potentials. https://www.ipcc.ch/report/ar5/

[32] M. Doninelli, E. Morosini, G. Di Marcoberardino, C.M. Invernizzi, P. Iora, Experimental characterization of CO_2–$SiCl_4$ mixture as innovative working fluid, Energy 299 (2024) 131197. https://doi.org/10.1016/j.energy.2024.131197

[33] F. Crespi, P. Rodríguez-de-Arriba, D. Sánchez, L. García-Rodríguez, Principles of operational optimization of CSP plants based on carbon dioxide mixtures, Appl. Therm. Eng. 260 (2025) 124871. https://doi.org/10.1016/j.applthermaleng.2024.124871

[34] Q. Deng, A. Liu, J. Li, Z. Feng, A review on supercritical CO_2 and CO_2-based mixture in power cycle, Energy Convers. Manag. 324 (2025) 119295. https://doi.org/10.1016/j.enconman.2024.119295

[35] Coco-Enríquez, L. *Nueva Generación de Centrales Termosolares con Colectores Solares Lineales Acoplados a Ciclos Supercríticos de Potencia*. Ph.D. Thesis, UPM, Spain, 2017.

[36] Dyreby, J.J. *Modeling the Supercritical Carbon Dioxide Brayton Cycle with Recompression*. Ph.D. Thesis, University of Wisconsin‑Madison, 2014 .

[37] Lemmon, E.W. *et al.*, NIST Standard Reference Database 23: REFPROP Version 10.0 (2018).

[38] Follett IV, W. W., Moore, J., Wade, J., & Pierre, S. (2024). The STEP 10 MWe sCO_2 pilot installation and commissioning status update. In Proceedings of the 8th International Supercritical CO_2 Power Cycles Symposium (Paper #74), February 26–29, 2024, San Antonio, TX, USA.

Annex A: sCO$_2$ Blends Properties

Table 3: sCO$_2$-Kr blend properties

Working Fluid	Critical Temperature (K)	Critical Pressure (kPa)	Critical Density (Kg/m3)
100%CO$_2$	304.13	7377.3	467.6
90%CO2+10%Kr	296.01	7753.13	552.61
80%CO2+20%Kr	286.64	7771.48	629.92
70%CO2+30%Kr	276.78	7606.3	730.39
60%CO2+40%Kr	267.25	7292.65	803.87
50%CO2+50%Kr	258.61	7037.87	865.53
40%CO2+60%Kr	250.39	6824.97	914.02
30%CO2+70%Kr	243.23	6708.85	878.59
20%CO2+80%Kr	235.22	6645.67	888.93
10%CO2+90%Kr	224.88	6388.89	922.15
100%Kr	209.48	5525	909.21

Table 4: sCO$_2$-R14(CF$_4$) blend properties

Working Fluid	Critical Temperature (K)	Critical Pressure (kPa)	Critical Density (Kg/m3)
100%CO2	304.13	7377.3	467.6
90%CO2+10%R14	295.93	7682.69	521.46
80%CO2+20%R14	286.01	7582.63	571.51
70%CO2+30%R14	275.41	7199.22	616.31
60%CO2+40%R14	264.76	6590.9	649.45
50%CO2+50%R14	254.78	5872.33	662.53
40%CO2+60%R14	245.91	5176.98	656.93
30%CO2+70%R14	238.43	4597.8	643.12
20%CO2+80%R14	242.83	4475.46	618.82
10%CO2+90%R14	229.17	3921.62	620.56
100%R14	227.51	3750	625.7

Table 5: sCO2-NF3 blend properties

Working Fluid	Critical Temperature (K)	Critical Pressure (kPa)	Critical Density (Kg/m3)
100%CO2	304.13	7377.3	467.6
90%CO2+10%NF3	296.59	7735.27	504.95
80%CO2+20% NF3	287.39	7651.58	539.54
70%CO2+30% NF3	277.69	7282.4	567.07
60%CO2+40% NF3	268.18	6735.24	583.34
50%CO2+50% NF3	259.4	6137.56	587.66
40%CO2+60% NF3	251.68	5590.62	584.18
30%CO2+70% NF3	245.25	5148.83	577.49
20%CO2+80% NF3	240.21	4824.3	569.05
10%CO2+90% NF3	236.52	4604.19	561.11
100%NF3	234	4460.7	562.47

Table 6: sCO2-CH4 blend properties

Working Fluid	Critical Temperature (K)	Critical Pressure (kPa)	Critical Density (Kg/m3)
100%CO2	304.13	7377.3	467.6
90%CO2+10%CH4	296.5	8081.61	450.88
80%CO2+20%CH4	287.26	8566.79	436.86
70%CO2+30%CH4	276.99	8889.2	420.02
60%CO2+40%CH4	265.44	8955.31	401.06
50%CO2+50%CH4	252.65	8692.27	379.14
40%CO2+60%CH4	239.13	8027.37	347.91
30%CO2+70%CH4	226.18	7111.83	301.24
20%CO2+80%CH4	213.59	6135.04	248.62
10%CO2+90%CH4	201.45	5261.42	198.44
100%CH4	190.564	4599.2	162.66

Annex B: Recompression Brayton Power Cycle Results

Table <mark>X</mark>: UA_LT(kW/K) 1550, UA_HT(kW/K) 1950, UA_Total(kW/K) 3500

CIT (ºC)	Working Fluid	CIT (K) Tcr	CIP (kPa) Pcr	Cycle Efficiency (%)	HT Pinch Point (K)	LT Pinch Point (K)
35	100%CO_2	308.15	8500	45.68	3.97	6.18
23.44	90%CO_2+10%NF_3					
14.24	80%CO_2+20%NF_3					
4.54	70%CO_2+30%NF_3					
-4.97	60%CO_2+40%NF_3					
-13.75	50%CO_2+50%NF_3					
-21.47	40%CO_2+60%NF_3					
-27.9	30%CO_2+70%NF_3					
-32.94	20%CO_2+80%NF_3					
-36.63	10%CO_2+90%NF_3					
-39.15	100%NF_3	234	4460.7	53.15	10.41	34.39