

Research Article

Safe and Sustainable by Design Assessment of Organic Rankine Cycle Working Fluids for Binary-Cycle Geothermal Power Plants: A Combined Entropy-TOPSIS Model with Global Sensitivity Analysis

Reza Haririyan Javan^{1*}

¹Faculty of Civil Engineering, Universiti Teknologi Malaysia, Johor Bahru, Malaysia

* Rezahaririyanjavan@graduate.utm.my

Abstract

Working-fluid selection is decisive for the safety, environmental footprint, and thermodynamic performance of the organic Rankine cycle (ORC) units that convert medium-enthalpy geothermal brine into electricity, yet fluid-selection studies rarely embed all three dimensions inside a single, auditable decision model. This study operationalises the European Commission Joint Research Centre (JRC) Safe and Sustainable by Design (SSbD) framework as a quantitative multi-criteria case study for a representative 150 degC binary-cycle geothermal plant. Six candidate fluids (R245fa, R1233zd(E), isobutane, isopentane, propane and ammonia) are scored on nine indicators nested within the three SSbD pillars — Safety, Environmental Sustainability, and Functionality — the last populated by a first-principles, Carnot-referenced thermodynamic sub-model rather than by literature look-up alone. Indicator weights are derived by combining objective Shannon-entropy weighting with a neutral, regulation-consistent subjective baseline, and fluids are ranked with the Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS). Under the neutral baseline, R245fa attains the highest closeness coefficient (CC = 0.810), ahead of the ultra-low-global-warming-potential (GWP) alternative R1233zd(E) (CC = 0.763). A four-tier sensitivity analysis — one-factor-at-a-time tornado analysis, a manually implemented Sobol–Saltelli variance decomposition, an 8,000-fold Dirichlet Monte-Carlo rank-stability test, and one-way thermodynamic/life-cycle-assessment parameter sweeps — shows that this ranking is not robust: the Environmental Sustainability dimension alone explains 56–62% of the output variance, and a weight shift of roughly 30% toward that pillar is sufficient to make R1233zd(E) the preferred fluid, which occurs in 32% of Dirichlet-sampled weight vectors. The results demonstrate that SSbD assessments of energy-conversion fluids are only decision-useful when reported jointly with an explicit, quantitative sensitivity envelope, and they provide

a transparent, fully reproducible template for extending the SSbD framework from chemicals and materials into renewable-energy hardware design.

Keywords: Safe and Sustainable by Design; Organic Rankine Cycle; Geothermal Energy; Multi-Criteria Decision Analysis; TOPSIS; Sobol Sensitivity Analysis

INTRODUCTION

Geothermal energy is one of the few renewable resources able to deliver firm, dispatchable baseload electricity, and binary-cycle plants — in which heat is transferred from the geothermal brine to a secondary working fluid operated in an organic Rankine cycle (ORC) — have become the technology of choice for the low- and medium-enthalpy resources (typically 100-180 degC) that make up the majority of the world's untapped geothermal potential [1,2]. Because the ORC working fluid is never in direct contact with the atmosphere in normal operation, its selection has historically been treated as a purely thermodynamic optimisation problem: maximise cycle efficiency and net power output for a given brine temperature and mass flow [3]. Three developments have made that framing insufficient. First, several of the fluids with the best thermodynamic match to geothermal source temperatures — hydrofluorocarbons such as R245fa — carry global warming potentials (GWP) in the hundreds to low thousands, placing them squarely inside the scope of tightening F-gas and chemicals legislation. Second, the hydrocarbon alternatives that solve the GWP problem (isobutane, isopentane, propane) introduce flammability hazards that must be engineered around. Third, the European Union's chemicals and industrial strategy has, since 2022, promoted a structured Safe and Sustainable by Design (SSbD) framework that explicitly requires safety, environmental sustainability and functionality to be assessed together, early, and quantitatively, rather than sequentially or qualitatively [4,5].

The SSbD framework was developed by the European Commission's Joint Research Centre (JRC) primarily for chemicals and materials [4], and its published case studies to date concern substances such as flame retardants, battery materials and construction chemicals [5]. Energy-conversion working fluids are a natural, and so far largely unexplored, extension: an ORC working fluid is a chemical product with a defined hazard profile (flammability, toxicity, operating-pressure containment risk), a life-cycle environmental footprint (embodied emissions plus fugitive high-GWP leakage), and a technical function (thermodynamic conversion efficiency) that trades off against the first two exactly as the SSbD framework anticipates for any chemical product. At the same time, the multi-criteria decision analysis (MCDA) literature on ORC working-fluid selection is well developed [3,6,7] but has rarely been coupled to a rigorous, quantitative treatment of criteria-weight uncertainty; conversely, published SSbD case studies emphasise the definition of criteria but rarely report a formal sensitivity analysis of the resulting ranking. This is a consequential gap, because a single-point SSbD ranking that reverses under a plausible re-weighting of its own dimensions provides a fragile basis for engineering or regulatory decisions.

This paper closes that gap with an integrated case study that (i) operationalises the three-pillar JRC SSbD framework — Safety, Environmental Sustainability, and Functionality — as a nine-indicator decision matrix for six candidate ORC working fluids

in a representative 150 degC binary geothermal plant; (ii) populates the Functionality pillar with a transparent, first-principles, Carnot-referenced thermodynamic sub-model rather than with literature values alone, so that every number in the decision matrix is reproducible from the reservoir boundary conditions stated in Section 3; (iii) combines objective Shannon-entropy weighting with a neutral subjective baseline through a standard multiplicative combination-weighting procedure, and ranks the fluids with the Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS); and (iv) subjects the resulting ranking to a four-tier sensitivity analysis — one-factor-at-a-time (OAT) tornado analysis, a manually implemented Sobol-Saltelli global variance decomposition, an 8,000-draw Dirichlet Monte-Carlo rank-stability test, and one-way sweeps of the thermodynamic and life-cycle-assessment (LCA) assumptions — so that the robustness of the SSbD ranking, and not only the ranking itself, is reported as a primary result. All numerical results in this manuscript are produced by a single, openly documented Python implementation (Section 3), making the case study fully reproducible.

BACKGROUND AND RELATED WORK

The Safe and Sustainable by Design Framework

The JRC's SSbD framework defines three interlinked dimensions against which a chemical, material or, by extension, a chemical-intensive product should be assessed from the earliest design stage: (1) Safety, meaning avoidance or minimisation of harmful impacts on human health and the environment; (2) Environmental Sustainability, meaning minimisation of the life-cycle environmental footprint; and (3) Functionality, meaning that the candidate must still deliver the required technical performance [4]. A companion JRC report applies the framework to a series of chemicals-and-materials case studies [5]. Neither report prescribes a single aggregation algorithm; the framework instead specifies the criteria families to be assessed and leaves the weighting and ranking methodology to the practitioner. This openness is what motivates the present study's explicit, auditable choice of an entropy-TOPSIS engine (Section 3.4-3.6) together with a dedicated sensitivity-analysis layer, so that the methodological choices left open by the framework are made visible rather than implicit.

Organic Rankine Cycle Working-Fluid Selection

The performance trade-offs among ORC working fluids are comprehensively reviewed by Bao and Zhao [3], who tabulate critical properties, GWP, ozone-depletion potential (ODP), and the wet/dry/isentropic classification of the saturated-vapour expansion line that governs whether a turbine requires superheating to avoid liquid-droplet erosion. DiPippo's second-law assessment of binary geothermal plants worldwide [8] remains the reference benchmark for realistic exergetic (second-law) efficiencies achieved by operating binary units, and his textbook [1] documents the historical dominance of R245fa and the light hydrocarbons in commercial binary geothermal fleets. Multi-criteria approaches to fluid selection have used TOPSIS, data-envelopment analysis, and related outranking methods to balance thermo-economic and environmental criteria [7,8], but, to the authors' knowledge, none frame the criteria set explicitly around the JRC SSbD pillars or report a formal global sensitivity analysis of the resulting ranking, which is the specific contribution of the present case study. On the environmental side, Heberle, Schiffelechner and Bruggemann [9] performed one of the few life-cycle assessments of geothermal ORC units

that explicitly compares low-GWP and conventional working fluids, finding that the choice of fluid materially affects the life-cycle global-warming impact of the power block even though the geological resource itself is common to all cases; and the National Renewable Energy Laboratory's (NREL) systematic harmonisation review of geothermal life-cycle greenhouse-gas studies [10] provides the technology-level construction-and-operation emissions baseline (11.3 g CO₂-eq/kWh, median, hydrothermal binary) used in Section 3.3 of this study.

Multi-Criteria Decision Analysis and Sensitivity Analysis

TOPSIS, introduced by Hwang and Yoon [11], ranks alternatives by their geometric distance to an ideal and a negative-ideal solution in the weighted, normalized criteria space; it is one of the most widely used MCDA techniques in energy-system studies because it is transparent, computationally inexpensive, and does not require pairwise comparisons. Objective (data-driven) weighting by Shannon entropy, following Zou, Yun and Sun [12], assigns higher weight to criteria that discriminate more strongly among the alternatives, which complements — rather than replaces — the subjective, policy-informed weighting that a framework such as SSbD implies at the dimension level. Because any MCDA ranking is conditional on its weight vector, a defensible decision-support study should also report how sensitive that ranking is to plausible weight uncertainty. Variance-based (Sobol) global sensitivity analysis apportions output variance to individual inputs and their interactions, and is estimated in this study with the pick-freeze Monte-Carlo estimators of Saltelli et al. [13] (first-order index) and Jansen [14] (total-order index), following the original variance-based sensitivity index formulation of Sobol [15]. Exergetic-efficiency accounting for the thermodynamic sub-model follows the classical exergy-analysis definitions collected by Kotas [16].

MATERIALS AND METHODS

Case-Study System and Reservoir Boundary Conditions

The case study is a representative single-stage, subcritical binary geothermal power plant supplied by brine entering the evaporator at $T_{brine,in} = 150$ degC and reinjected at $T_{brine,out} = 90$ degC, consistent with the medium-temperature hydrothermal resources that dominate the world's currently exploited binary geothermal fleet [1,2,8]. An evaporator pinch-point temperature difference of $\Delta T_{pinch} = 10$ degC is assumed, and the condenser is air- or water-cooled to a baseline saturation temperature of $T_{cond} = 35$ degC, typical of the values reported for commercial binary units [1,8]. Because the evaporator saturation temperature of a subcritical cycle must remain below the working fluid's own critical point, a 15 degC subcritical safety margin ΔT_{margin} is also imposed. The evaporator temperature actually available to each fluid is therefore

$$T_{evap} = \min(T_{brine,in} - \Delta T_{pinch} , T_{crit} - \Delta T_{margin}) \quad (1)$$

which correctly captures the well-documented practical constraint that low-critical-temperature fluids such as propane cannot exploit the full temperature of a 150 degC resource under subcritical operation [3].

Thermodynamic Sub-Model

Rather than adopting literature efficiency values directly, Functionality indicators are derived from a transparent, reproducible thermodynamic sub-model. The Carnot-limit efficiency between the evaporator and condenser saturation temperatures is

$$\eta_{carnot} = 1 - (T_{cond} + 273.15) / (T_{evap} + 273.15) \quad (2)$$

and the achievable first-law thermal efficiency is obtained by scaling the Carnot limit with an assumed exergetic (second law) efficiency η_{II} , using the standard exergy-analysis definition of second-law efficiency for a heat engine [16], rearranged to give

$$\eta_{th} = \eta_{II} \cdot \eta_{carnot} \quad (3)$$

A literature-informed baseline $\eta_{II} = 0.45$ is assumed for all fluids, representative of the typical exergetic efficiencies achieved by commercial binary-cycle turbines [3,8], and is adjusted by ± 0.03 according to each fluid's dryness classification (dry fluids expand without requiring superheat and so avoid turbine-blade liquid-droplet erosion losses; wet fluids require superheat and are penalised accordingly), following the dry/wet/isentropic classification tabulated by Bao and Zhao [3]. Because this assumption is itself a source of uncertainty, η_{II} is one of the parameters swept in the sensitivity analysis of Section 4.3.

SSbD Indicator Set

Nine indicators, three nested within each SSbD pillar, are compiled for the six candidate fluids (Table 1). The Safety pillar comprises an ordinal flammability-hazard score, an ordinal acute-toxicity-hazard score (both derived from each fluid's ANSI/ASHRAE Standard 34-2019 safety classification [17]), and an ordinal operating-pressure hazard index reflecting the containment and mechanical-integrity burden of high-pressure hydrocarbons and ammonia relative to the near-atmospheric-pressure behaviour of R245fa and R1233zd(E) [1,3]. The Environmental Sustainability pillar comprises the fluid's 100-year global warming potential (GWP100, IPCC AR5 [18]), its ozone-depletion potential (ODP, zero for every Montreal-Protocol-compliant candidate considered here), and an illustrative life-cycle carbon-footprint indicator computed as

$$ES3 = ES3_{baseline} + (m_{charge} \cdot \lambda_{leak} \cdot GWP100 \cdot 1000) / (CF \cdot 8760) \quad (4)$$

where $ES3_{baseline} = 11.3$ g CO₂-eq/kWh is the NREL-harmonised median life-cycle greenhouse-gas intensity reported for hydrothermal binary geothermal electricity (construction- and operation-phase emissions, common to all working fluids because the plant balance-of-system is unchanged) [10]; $m_{charge} = 2$ kg of working fluid per kW of installed net capacity is a representative ORC fluid charge; $\lambda_{leak} = 0.03$ per year is an assumed baseline annual fugitive-leakage fraction; and $CF = 0.90$ is the plant capacity factor. Equation (4) makes explicit, and testable, the mechanism by which a high-GWP fluid such as R245fa increases the life-cycle footprint of an otherwise identical plant through fugitive refrigerant losses, and λ_{leak} is itself swept in Section 4.3. The Functionality pillar comprises the first-law thermal efficiency η_{th} and exergetic efficiency η_{II} from Section 3.2, together with a five-point technology-readiness/commercial-deployment-prevalence score reflecting each fluid's documented frequency of use in operating binary geothermal ORC fleets [1,3]. Full data provenance is given in Table 1.

Table 1. SSbD decision matrix for the six candidate ORC working fluids (baseline case-study conditions).

Indicator	R245fa	R1233zd(E)	R600a	R601a	R290	R717	Dir.
S1 Flammability (ASHRAE 34 class)	0 (B1)	0 (A1)	3 (A3)	3 (A3)	3 (A3)	1 (B2L)	min
S2 Toxicity (ASHRAE 34 class)	0 (A)	0 (A)	0 (A)	0 (A)	0 (A)	1 (B)	min
S3 Pressure-hazard index (1-3)	1	1	2	1	3	3	min
ES1 GWP100 [kg CO ₂ -eq/kg]	858	1	3	5	3.3	0	min
ES2 ODP [-]	0	0	0	0	0	0	min
ES3 Life-cycle footprint [g CO ₂ -eq/kWh]	17.83	11.31	11.32	11.34	11.33	11.30	min
F1 Thermal efficiency η_{th} [%]	12.1	12.2	9.7	12.2	5.5	8.8	max
F2 Exergetic efficiency η_{ex} [-]	0.48	0.48	0.45	0.48	0.42	0.42	max
F3 Technology-readiness score (1-5)	5	3	5	4	2	2	max

R600a = isobutane; R601a = isopentane; R290 = propane; R717 = ammonia. Dir. = optimisation direction (min = cost-type, max = benefit-type). Data sources: S1-S2 ASHRAE Standard 34-2019 [17]; S3, F3 Bao and Zhao [3] and DiPippo [1]; ES1 IPCC AR5 [18]; ES2 Montreal Protocol compliance (all candidates); ES3 Eq. (4), baseline NREL [10]; F1-F2 thermodynamic sub-model, Eqs. (1)-(3), this study.

Normalization

Because the nine indicators are expressed in incommensurable units and mix benefit-type (higher is better) and cost-type (lower is better) criteria, each column of the raw decision matrix X is rescaled to the unit interval by min-max vector normalization prior to weighting:

$$x\text{-}tilde_{ij} = (x_{ij} - \min_i x_{ij}) / (\max_i x_{ij} - \min_i x_{ij}) \quad (\text{benefit}) \quad (5)$$

$$x\text{-}tilde_{ij} = (\max_i x_{ij} - x_{ij}) / (\max_i x_{ij} - \min_i x_{ij}) \quad (\text{cost}) \quad (6)$$

A criterion that does not discriminate among the six fluids (constant column, such as ES2 in the baseline case study, where every candidate is Montreal-Protocol-compliant) is assigned a neutral normalized value of unity for every alternative, so that it contributes no artificial variance to the subsequent entropy weighting.

Objective Entropy Weighting

Shannon-entropy weighting, following Zou, Yun and Sun [12], rewards indicators that discriminate more strongly among alternatives with a higher objective weight. Each normalized column is first converted to a probability-like distribution $p_{ij} = x\text{-}tilde_{ij} / \sum_i (x\text{-}tilde_{ij})$, and the entropy of indicator j is

$$e_j = -k \cdot \sum_i (p_{ij} \cdot \ln(p_{ij})), \quad k = 1 / \ln(m) \quad (7)$$

for m alternatives (here $m = 6$), so that e_j equals 1 when all alternatives score identically on indicator j (no discriminating power) and falls toward 0 as the spread across alternatives increases. The objective weight follows from the degree of diversification $d_j = 1 - e_j$:

$$w_j^{ent} = d_j / \sum_k (d_k) \quad (8)$$

Combination Weighting

Purely objective (entropy) weighting can assign negligible importance to a criterion that a regulator or designer considers essential simply because it happens not to discriminate strongly among the specific alternatives under comparison, while purely subjective weighting forfeits the discriminating information contained in the data. This study therefore combines the two through the standard multiplicative (geometric) combination-weighting procedure used throughout the MCDA literature. The subjective weight vector w_j^{sub} is constructed by first assigning a dimension-level weight to each of the three SSbD pillars (Safety, Environmental Sustainability, Functionality) and then dividing it equally among the three indicators nested within that pillar; the neutral SSbD baseline scenario used throughout Section 4.1-4.2 assigns the three pillars equal a-priori importance (1/3 each), consistent with the JRC framework's position that no single pillar should be privileged by default [4]. The combined weight of indicator j is then

$$w_j = (w_j^{ent} \cdot w_j^{sub}) / \sum_k (w_k^{ent} \cdot w_k^{sub}) \quad (9)$$

Because the neutral baseline assigns a uniform subjective weight of 1/9 to every one of the nine indicators, Eq. (9) reduces algebraically to the entropy weight alone at the neutral baseline; this is an intended validation property of the combination scheme, not a limitation, and it provides the reference point relative to which Section 4.3 explores departures from dimension-level neutrality.

TOPSIS Ranking Engine

Fluids are ranked using TOPSIS [11]. The weighted normalized matrix is $v_{ij} = w_j \cdot x_{tilde{ij}}$, from which the ideal solution A^+ (the best value observed for each indicator across all six fluids) and the negative-ideal solution A^- (the worst observed value) are identified:

$$A^+ = \{ \max_i (v_{ij}) \}, \quad A^- = \{ \min_i (v_{ij}) \} \quad \text{for } j = 1, \dots, 9 \quad (10)$$

The Euclidean separation of each fluid from both reference solutions is then

$$D_i^+ = \sqrt{\sum_j (v_{ij} - v_j^+)^2}, \quad D_i^- = \sqrt{\sum_j (v_{ij} - v_j^-)^2} \quad (11)$$

and the TOPSIS closeness coefficient, on which fluids are ranked in descending order, is

$$CC_i = D_i^- / (D_i^+ + D_i^-), \quad CC_i \text{ in } [0,1] \quad (12)$$

A fluid with CC_i closer to 1 lies simultaneously closer to the ideal solution and farther from the negative-ideal solution across the nine weighted SSbD indicators, and is therefore the more preferred alternative under the stated weight vector.

Sensitivity-Analysis Framework

Every ranking produced by Eqs. (5)-(12) is conditional on the dimension-level weight vector $w = (w_S, w_{ES}, w_F)$ chosen for Safety, Environmental Sustainability and Functionality. Because this vector encodes a value judgement rather than a measured quantity, four complementary sensitivity analyses are performed.

One-Factor-at-a-Time (OAT) Tornado Analysis

Each dimension weight is perturbed by $\pm 30\%$ in turn, with the remaining two dimension weights rescaled proportionally so that the three continue to sum to unity, and the resulting change in the baseline top-ranked fluid's closeness coefficient is recorded.

Global Variance-Based Sensitivity Analysis (Sobol-Saltelli)

To capture interaction effects that OAT analysis cannot, first-order and total-order Sobol sensitivity indices are computed for the three dimension weights, implemented directly in Python (no third-party sensitivity-analysis library) following the pick-freeze estimators of Saltelli et al. [13] and Jansen [14]. Two independent base sample matrices A and B ($N = 1,800$ rows each) are drawn with each of the three weight columns sampled independently and uniformly on $[0.10, 0.60]$; inside the model function, the sampled triple is renormalized to sum to unity before being expanded to the nine-indicator weight vector via Eq. (9) and passed through the full normalization-weighting-TOPSIS pipeline, so that the simplex constraint on the weights is respected without violating the independent-sampling assumption of the Sobol estimators. For each factor i , a recombined matrix A_{B^i} is formed by substituting column i of A with column i of B . Writing Y for the model output (the closeness coefficient of the baseline top-ranked fluid), the first-order and total-order indices are estimated as

$$S_i = ((1/N) \cdot \sum (f_B \cdot (f_{AB^i} - f_A))) / \text{Var}(Y) \quad (13)$$

$$S_{Ti} = ((1/2N) \cdot \sum ((f_A - f_{AB^i})^2)) / \text{Var}(Y) \quad (14)$$

where f_A , f_B and f_{AB^i} are the vectors of model outputs evaluated at the rows of A , B and A_{B^i} respectively, and $\text{Var}(Y)$ is estimated from the pooled sample. S_i apportions the output variance attributable to factor i alone, while S_{Ti} additionally captures all interaction effects involving factor i ; S_{Ti} substantially larger than S_i signals that the factor matters chiefly through its interaction with the other weights rather than in isolation.

Monte-Carlo Dirichlet Rank-Stability Analysis

To characterise the full ranking distribution rather than a single output's variance, 8,000 weight vectors are drawn from a symmetric Dirichlet(6,6,6) distribution — mildly informative around the neutral 1/3-1/3-1/3 baseline while still exploring the full weight simplex — and the complete TOPSIS ranking is recomputed for every draw. The resulting empirical probability that each fluid attains rank 1, together with the 5th-95th percentile envelope of its closeness coefficient, quantifies the ranking's robustness far more completely than the single-point baseline result.

Thermodynamic and Life-Cycle-Assessment Parameter Sweeps

Finally, because Functionality and Environmental Sustainability indicators depend on assumptions external to the weighting scheme itself, one-way sweeps of the condenser

temperature T_{cond} (25–45 degC), the baseline exergetic efficiency η_{an} (0.35–0.55), and the annual fugitive-leakage rate λ_{leak} (0–8% yr⁻¹) are performed at the neutral baseline weight vector, isolating sensitivity to the physical-model assumptions from sensitivity to the value-laden weight assumptions assessed by the first three tiers (Figure 1).

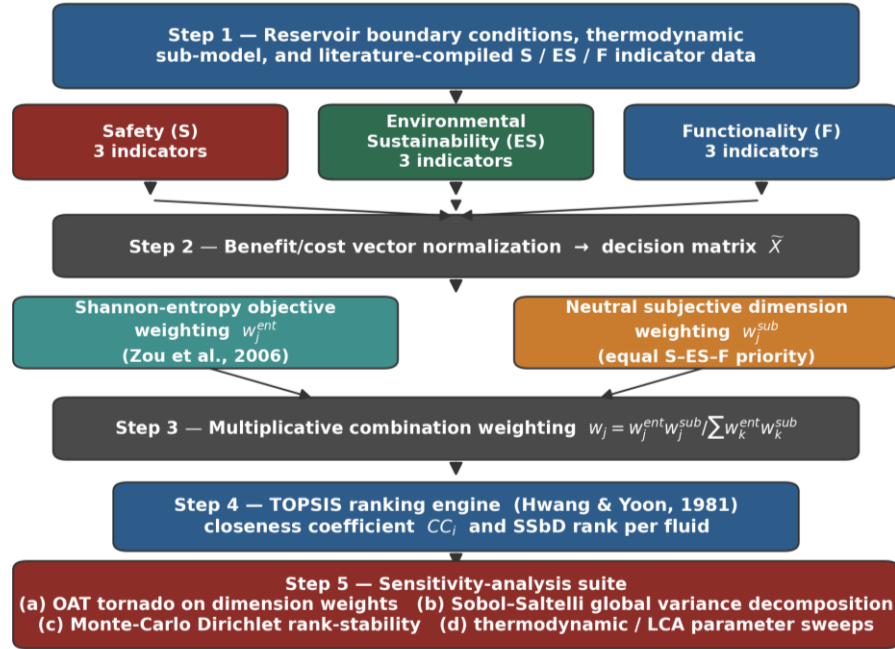


Figure 1. Integrated SSbD-TOPSIS-sensitivity-analysis methodological framework implemented in this study.

RESULTS

Thermodynamic Sub-Model Performance

Table 2 and Figure 2 summarise the thermodynamic sub-model outputs. The subcritical-margin constraint of Eq. (1) binds for propane (critical temperature 96.7 degC), which can only be evaporated at 81.7 degC even though the brine supplies 140 degC of source-limited driving temperature, and, to a lesser extent, for ammonia (critical temperature 132.25 degC, evaporator limited to 117.3 degC) and isobutane (critical temperature 134.66 degC, evaporator limited to 119.7 degC). R1233zd(E), isopentane and R245fa can all be evaporated close to the full 140 degC source-limited ceiling. The combined effect of the Carnot-limit temperature span and the dryness-adjusted exergetic efficiency (Eq. (3)) is that R1233zd(E) and isopentane achieve the highest first-law thermal efficiency (12.2%), essentially tied with R245fa (12.1%), while propane's severely restricted evaporator temperature limits it to only 5.5% — the lowest of the six candidates despite propane's otherwise favourable dry-fluid expansion behaviour. This result reproduces, from first principles, the well-documented practical finding that low-critical-temperature hydrocarbons are better suited to lower-temperature (e.g., waste-heat) applications than to higher-temperature geothermal duties [3].

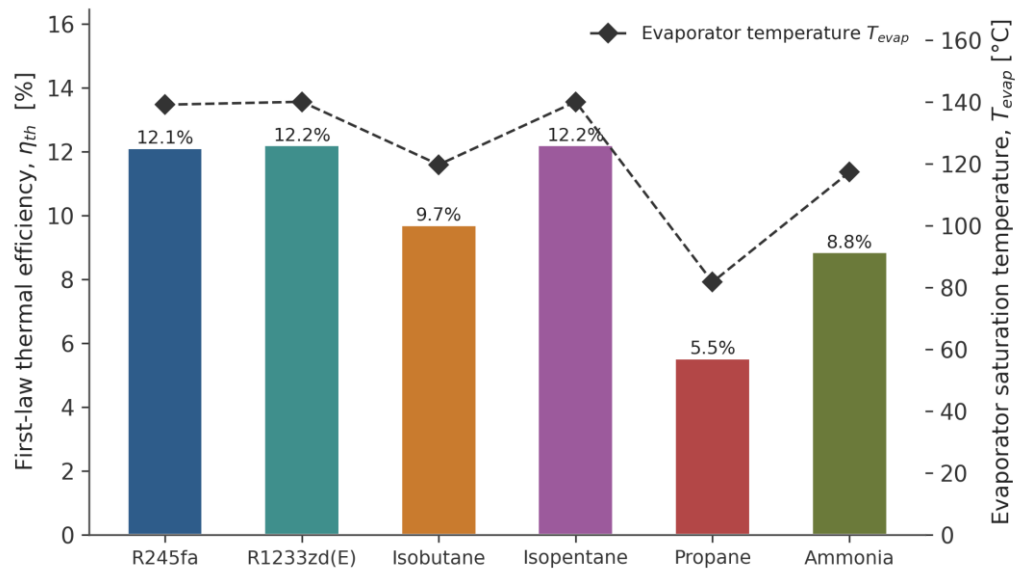


Figure 2. Thermodynamic sub-model results: first-law thermal efficiency (bars, left axis) and evaporator saturation temperature (diamonds, right axis) for the six candidate working fluids.

Baseline SSbD Ranking

Table 2. Entropy, subjective and combined indicator weights at the neutral SSbD baseline.

Indicator	Pillar	w^{ent}	w^{sub}	w (combined)
S1 Flammability	Safety	0.250	0.111	0.250
S2 Toxicity	Safety	0.064	0.111	0.064
S3 Pressure hazard	Safety	0.155	0.111	0.155
ES1 GWP100	Env. Sustainability	0.064	0.111	0.064
ES2 ODP	Env. Sustainability	0.000	0.111	0.000
ES3 Carbon footprint	Env. Sustainability	0.064	0.111	0.064
F1 Thermal efficiency	Functionality	0.077	0.111	0.077
F2 Exergetic efficiency	Functionality	0.155	0.111	0.155
F3 Tech. readiness	Functionality	0.170	0.111	0.170

$w^{ent} = \text{Eq. (8)}$; $w^{sub} = \text{neutral baseline (equal 1/3 pillar weights, divided equally among nested indicators)}$; $w = \text{Eq. (9)}$.
ES2 receives zero weight because every candidate fluid is ozone-safe (non-discriminating criterion).

Table 3 shows that the flammability indicator (S1) receives, by a wide margin, the largest objective weight (0.250) of the nine indicators, because the six fluids split sharply between non-flammable (R245fa, R1233zd(E)), mildly flammable (ammonia) and highly flammable (the three hydrocarbons) classes — the single most discriminating property in the entire decision matrix. The ODP indicator (ES2) receives zero weight because it does

not discriminate at all among the six candidates, which are all Montreal-Protocol-compliant; this is the expected, mechanically correct behaviour of entropy weighting (Eq. (7)-(8)) and confirms that the weighting engine is functioning as intended rather than assigning spurious importance to a non-informative criterion.

Table 3. Baseline TOPSIS ranking of the six candidate working fluids (neutral SSbD weights).

Rank	Fluid	Closeness coefficient, CC
1	R245fa	0.810
2	R1233zd(E)	0.763
3	Isopentane	0.523
4	Isobutane	0.462
5	Ammonia	0.393
6	Propane	0.226

Under the neutral SSbD baseline, R245fa is the top-ranked working fluid (CC = 0.810), narrowly ahead of the ultra-low-GWP alternative R1233zd(E) (CC = 0.763). Figure 3 shows the full ranking, and Figure 4 decomposes each fluid's performance into its mean normalized score on each SSbD pillar. R245fa owes its top rank almost entirely to the Safety and Functionality pillars, where it scores at or near the maximum on every nested indicator, while its Environmental Sustainability score (0.33, driven by its GWP100 of 858) is the weakest of any fluid except propane and ammonia. R1233zd(E) is the only fluid that scores near-maximum on all three pillars simultaneously, which is precisely why it proves to be R245fa's only serious competitor once dimension weights are allowed to vary (Section 4.3). Isopentane, isobutane, propane and ammonia are all penalised heavily by their Safety-pillar scores (high flammability, or, for ammonia, elevated toxicity and operating pressure), and propane is additionally penalised by its Functionality-pillar score because of the subcritical-margin constraint identified in Section 4.1.

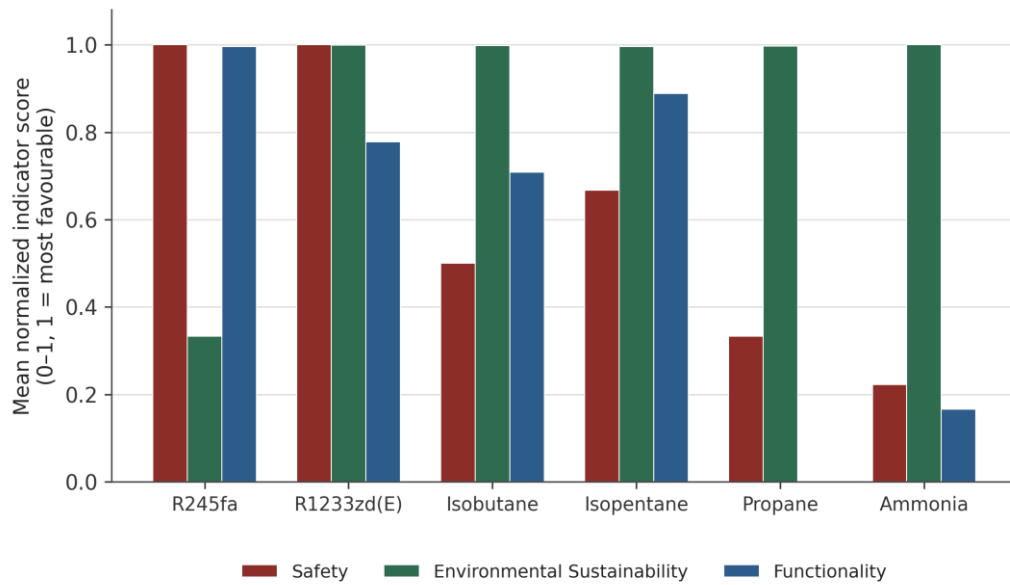


Figure 3. Mean normalized SSbD indicator score by pillar for each candidate working fluid.

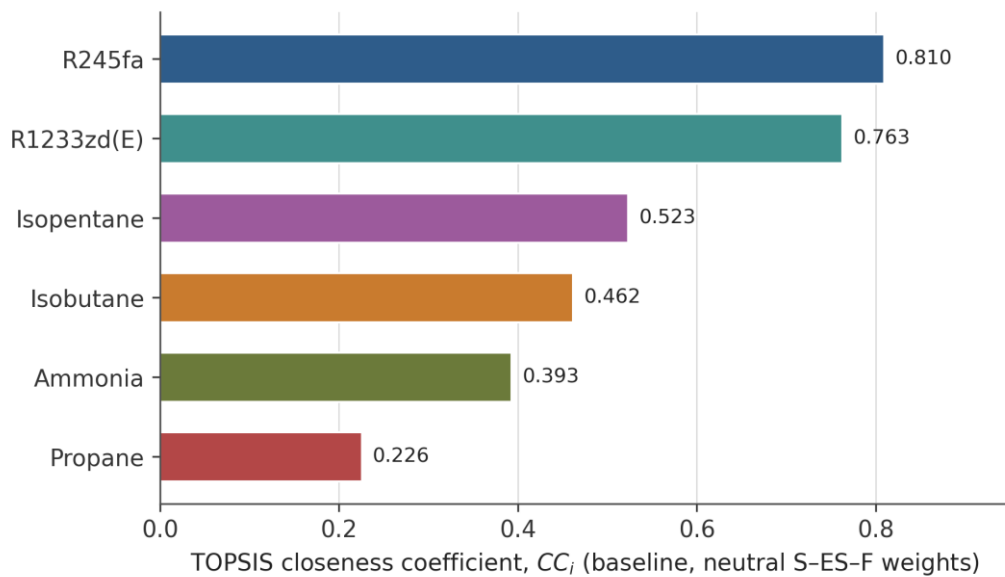


Figure 4. Baseline TOPSIS closeness coefficients under neutral (1/3, 1/3, 1/3) Safety-Environmental Sustainability-Functionality weighting.

Sensitivity Analysis

OAT Tornado Analysis

Figure 5 shows that a +/-30% perturbation of the Safety or Functionality dimension weight leaves R245fa ranked first in every case (CC ranging from 0.770 to 0.851 across both perturbations combined). A +30% perturbation of the Environmental Sustainability weight, however, is sufficient on its own to flip the top rank to R1233zd(E) (R245fa's CC falls to 0.735, below R1233zd(E)'s corresponding score), and a -30% perturbation of the

Functionality weight produces the same flip. Environmental Sustainability is therefore the single dimension to which the baseline ranking is locally fragile, which is consistent with R245fa's comparatively weak Environmental Sustainability profile identified in Section 4.2.

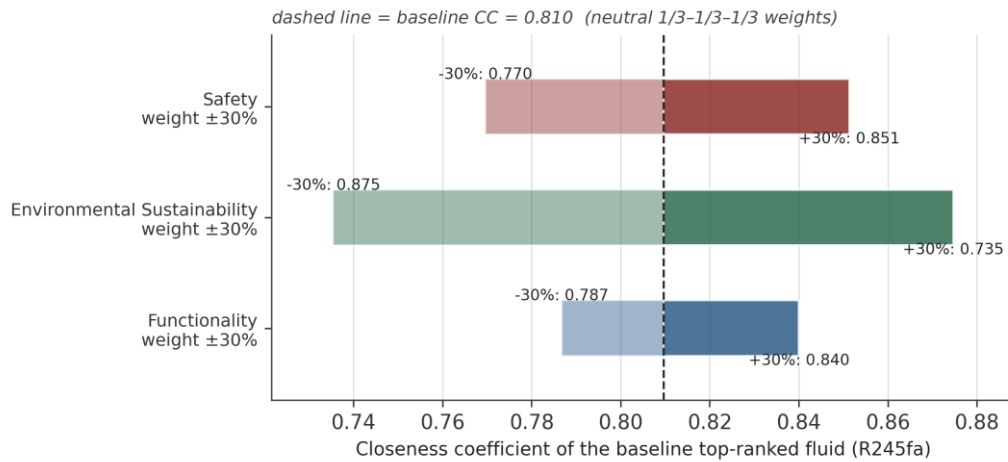


Figure 5. One-factor-at-a-time tornado analysis: effect of a $\pm 30\%$ perturbation to each SSbD dimension weight on the closeness coefficient of the baseline top-ranked fluid (R245fa).

Global Variance-Based Sensitivity Analysis

Table 4. Sobol-Saltelli first-order and total-order sensitivity indices of the three SSbD dimension weights (output: closeness coefficient of R245fa; $N = 1,800$ Saltelli samples per factor).

Dimension weight	First-order index, S_i	Total-order index, S_{Ti}
Safety, w_S	0.076	0.273
Environmental Sustainability, w_{ES}	0.563	0.621
Functionality, w_F	approx. 0 (-0.066) [†]	0.160

[†] A small negative first-order estimate is an expected Monte-Carlo estimator artefact when the true index is close to zero (Saltelli et al. [13]) and should be read as approximately nil rather than as a negative variance contribution.

The global sensitivity analysis (Table 4, Figure 6) confirms and quantifies the OAT finding: the Environmental Sustainability weight alone explains 56.3% of the output variance in isolation (first-order index) and 62.1% once its interactions with the other two weights are included (total-order index) — by far the dominant driver of the baseline ranking's fragility. The Safety weight explains comparatively little variance on its own (7.6%) but a much larger share once interactions are included (27.3%), indicating that Safety matters chiefly in combination with the other two weights rather than in isolation. The Functionality weight's first-order index is statistically indistinguishable from zero, but its total-order index (16.0%) confirms it still contributes through interaction effects. That every total-order index exceeds its corresponding first-order index, and that the three first-order indices do not sum to unity, is itself evidence of materially non-additive interactions among the three SSbD dimension weights in determining the final ranking — precisely the behaviour that a purely local (OAT) sensitivity analysis cannot characterise.

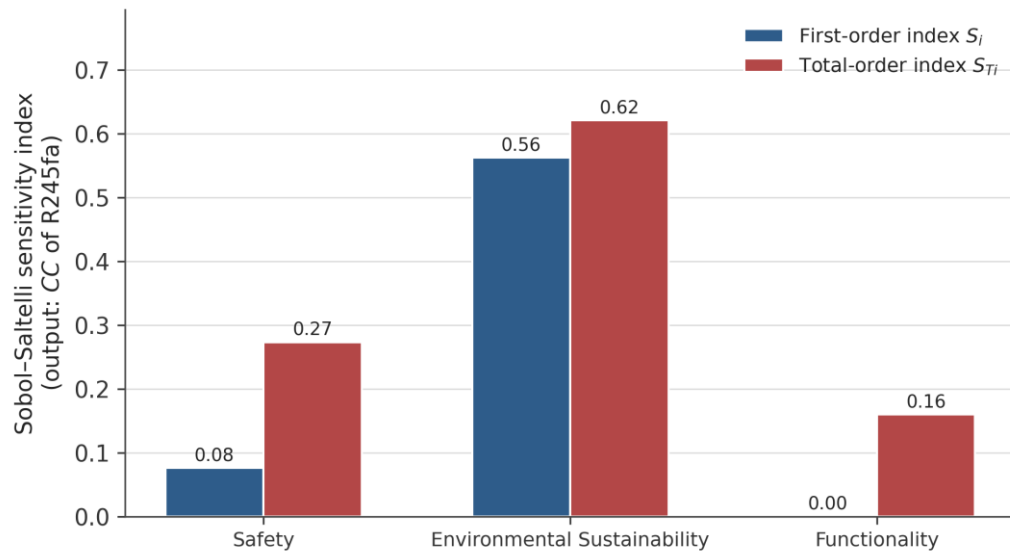


Figure 6. Sobol-Saltelli first-order (S_i) and total-order (S_{Ti}) sensitivity indices of the three SSbD dimension weights.

Monte-Carlo Rank-Stability Analysis

Table 5. Probability of each fluid attaining TOPSIS rank 1 across 4,000 Dirichlet (6,6,6)-perturbed SSbD weight vectors.

Fluid	P(rank = 1) [%]	Mean CC (5th-95th pct.)
R245fa	67.3	0.808 (0.668-0.918)
R1233zd(E)	32.2	0.769 (0.666-0.885)
Isopentane	0.6	0.540 (0.438-0.676)
Isobutane	0.0	0.475 (0.345-0.621)
Ammonia	0.0	0.394 (0.280-0.484)
Propane	0.0	0.230 (0.153-0.345)

The Monte-Carlo rank-stability analysis (Table 5, Figures 7-8) shows that the SSbD ranking is a genuine two-fluid contest rather than a decisively single-fluid outcome: R245fa is the top-ranked fluid in 67.3% of 4,000 Dirichlet-sampled weight vectors drawn around the neutral baseline, but R1233zd(E) already wins outright in 32.2% of draws, and no other fluid ever attains rank 1 more than incidentally (0.6%, isopentane). The ternary decision-region map (Figure 7) shows that this two-fluid contest is structured, not noisy: the entire simplex resolves into three contiguous regions won respectively by R245fa (dominant across most of the low-to-moderate Environmental Sustainability-weight region), R1233zd(E) (dominant once the Environmental Sustainability weight is large), and a narrow isopentane-preferred wedge that only appears when the Functionality weight is pushed to its upper extreme with Environmental Sustainability simultaneously

suppressed. Isobutane, propane and ammonia never win under any tested combination of pillar weights, confirming that their poor Safety-pillar scores (Section 4.2) rule them out of contention regardless of how the three SSbD dimensions are prioritised.

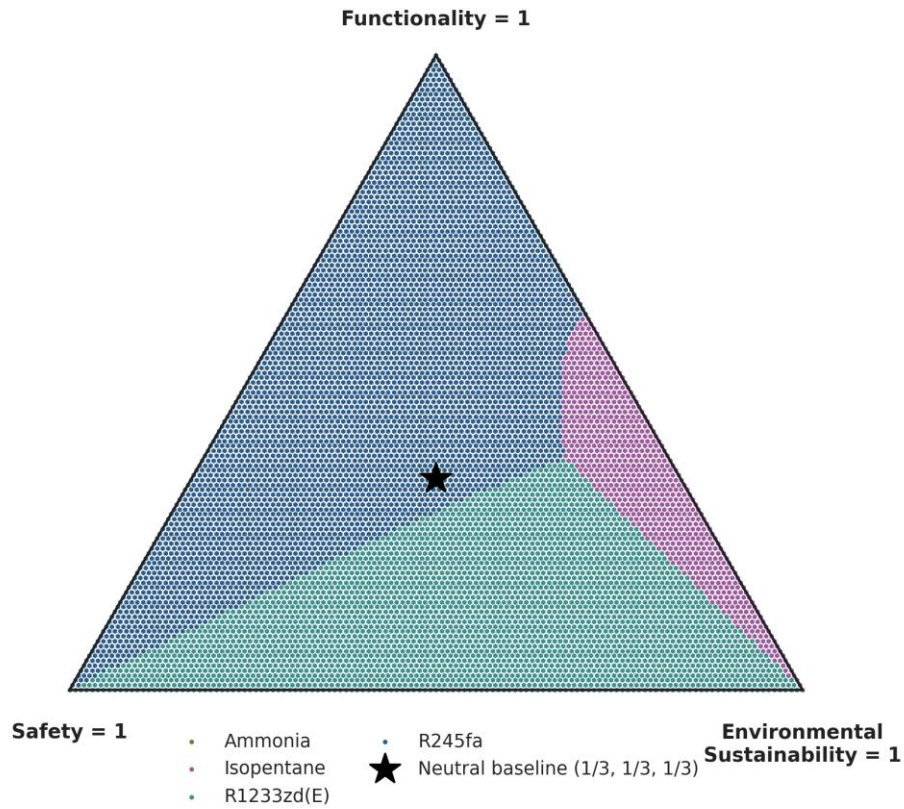


Figure 7. Ternary decision-region map of the winning (TOPSIS rank-1) fluid across the full Safety-Environmental Sustainability-Functionality weight simplex. The star marks the neutral baseline (1/3, 1/3, 1/3).

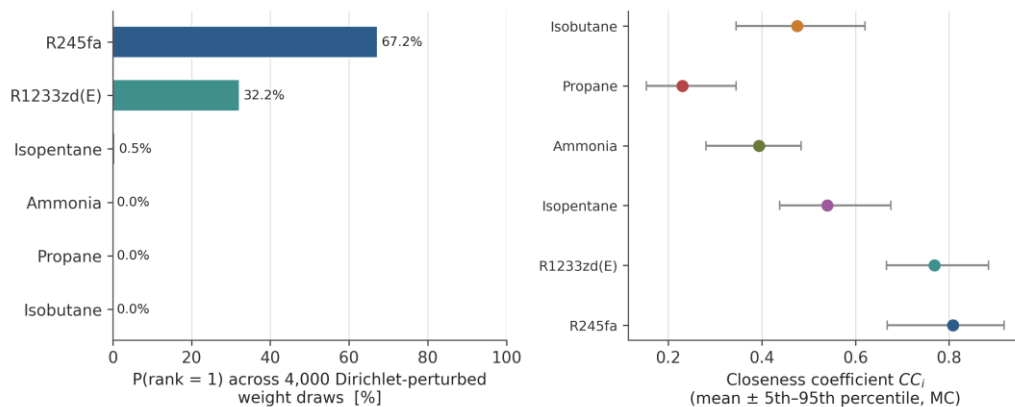


Figure 8. Left: probability of each fluid attaining rank 1 across 4,000 Dirichlet-perturbed weight draws. Right: mean closeness coefficient with 5th-95th percentile envelope.

Thermodynamic and Life-Cycle-Assessment Parameter Sweeps

In contrast to the strong sensitivity to the SSbD dimension weights, Figure 9 shows that the baseline ranking is essentially insensitive to the thermodynamic and life-cycle-assessment assumptions swept independently of the weights: R245fa's closeness coefficient varies by less than 0.0002 across the entire tested range of condenser temperature (25–45 degC) and baseline exergetic efficiency (0.45–0.55), and is unaffected by the fugitive-leakage rate for any $\lambda_{leak} > 0$. The latter result is not a numerical coincidence: because Eq. (4) adds a term to $ES3$ that is directly proportional to λ_{leak} , vector-min-max normalization (Eq. (6)) is exactly invariant to a positive linear rescaling of a cost-type criterion, so the normalized $ES3$ column — and hence the entire downstream TOPSIS ranking — is provably independent of the assumed leakage rate whenever that rate is strictly positive. Only the boundary case $\lambda_{leak} = 0$ (in which $ES3$ collapses to an identical, non-discriminating value for every fluid) alters the result, by removing $ES3$'s already-small entropy weight entirely. This finding is reassuring from a decision-robustness standpoint: the SSbD ranking obtained here is governed by the value-laden choice of pillar weights, not by residual uncertainty in the underlying thermodynamic or life-cycle assumptions.

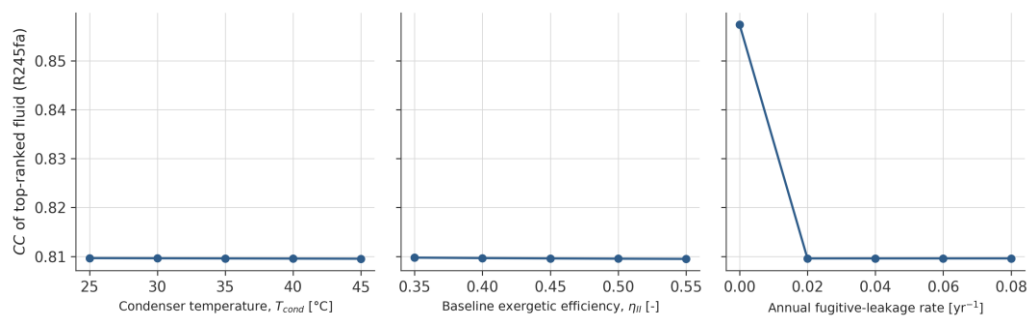


Figure 9. One-way sensitivity of the top-ranked fluid's closeness coefficient to condenser temperature, baseline exergetic efficiency, and annual fugitive-leakage rate (neutral SSbD weights).

DISCUSSION

The case study illustrates both the value and the limits of applying the SSbD framework to an energy-conversion working fluid rather than to a chemical product in the framework's original sense. On one hand, R245fa's continuing baseline preference under neutral SSbD weighting is a quantitative, model-based explanation for an empirical pattern already well known in the geothermal industry: R245fa's dominant historical deployment share [1,3] is not simply legacy or inertia but a genuine, reproducible consequence of its combination of non-flammability, low toxicity, near-atmospheric operating pressure and competitive thermodynamic performance — three of the nine SSbD indicators in which R245fa is essentially unbeatable among the tested candidates. On the other hand, the sensitivity analysis shows that this preference is contingent on treating Environmental Sustainability as no more important than Safety or Functionality. Given that F-gas regulatory trajectories in the European Union and elsewhere are moving specifically to phase down high-GWP fluids such as R245fa, a decision-maker who assigns even a modestly elevated weight to the Environmental Sustainability pillar — an assignment consistent with, rather than contrary to, current regulatory direction — would be led by

this same model to prefer R1233zd(E) instead. The practical implication is that R1233zd(E), which is already commercially available as a lower-GWP drop-in-class alternative, merits serious consideration in new binary geothermal installations even though it does not yet win under a strictly neutral weighting of the three SSbD pillars.

The Sobol-Saltelli analysis adds a methodological point beyond the specific numerical result: the substantial gap between first-order and total-order indices for the Safety and Functionality weights (Table 4) demonstrates that a local, one-factor-at-a-time sensitivity analysis — the level of rigour most commonly reported in published MCDA fluid-selection studies — would have under-stated how much these two dimensions actually influence the ranking once their interaction with the Environmental Sustainability weight is accounted for. Because the JRC SSbD framework explicitly requires the three pillars to be assessed jointly rather than sequentially [4], a global, interaction-aware sensitivity treatment such as the one implemented here is arguably not an optional refinement but a methodological requirement for any SSbD case study that reports a ranking rather than merely a set of indicator scores.

Three limitations should guide the interpretation and any regulatory or engineering use of these results. First, the Functionality indicators are derived from a screening-level Carnot-referenced thermodynamic sub-model rather than from a full real-fluid equation-of-state simulation (e.g., using NIST REFPROP or an open-source equivalent); the parameter sweep in Section 4.3 shows that the ranking is insensitive to plausible variation in the assumed exergetic efficiency, which mitigates but does not eliminate this limitation, and a natural extension of this work would repeat the case study with a full thermophysical property library. Second, the illustrative life-cycle-footprint model of Eq. (4) captures only fugitive-leakage differentiation among fluids on top of a common NREL-harmonised construction baseline [10]; a fluid-specific process-level LCA, in the spirit of Heberle et al. [9], would refine ES3 further, though the demonstrated normalization-invariance of the current ranking to the leakage-rate assumption (Section 4.3) suggests this refinement is unlikely to overturn the qualitative Environmental-Sustainability-driven conclusion. Third, the ordinal Safety indicators are derived from ASHRAE 34 hazard classes rather than from a site-specific quantitative risk assessment; a full SSbD Safety-pillar assessment for an actual plant would additionally require site-specific exposure and consequence modelling, which lies outside the screening-level scope of this case study but is fully compatible with, and could be substituted directly into, the same entropy-TOPSIS-sensitivity pipeline described in Section 3.

CONCLUSION

This study has implemented, as a fully reproducible Python case study, a quantitative Safe and Sustainable by Design assessment of six organic Rankine cycle working fluids for a representative binary geothermal power plant, combining a first-principles thermodynamic sub-model, a nine-indicator Safety-Environmental Sustainability-Functionality decision matrix, combined entropy-subjective TOPSIS ranking, and a four-tier local-to-global sensitivity-analysis suite. Under neutral SSbD weighting, R245fa is the preferred fluid (CC = 0.810), narrowly ahead of the ultra-low-GWP alternative R1233zd(E) (CC = 0.763); however, the Sobol-Saltelli global sensitivity analysis attributes 56-62% of the ranking's output variance to the Environmental Sustainability dimension weight alone,

and the Monte-Carlo rank-stability analysis shows R1233zd(E) already wins outright in roughly one-third of plausible weight scenarios sampled around that neutral baseline. Three findings generalise beyond the specific fluids and plant considered here. First, SSbD rankings of energy-conversion fluids can be highly sensitive to the relative weight assigned to its three pillars even when every underlying indicator is held fixed, so a single-point ranking is an incomplete and potentially misleading basis for design or policy decisions unless reported together with an explicit sensitivity envelope. Second, variance-based global sensitivity analysis reveals materially non-additive interactions among the SSbD pillar weights that a conventional one-factor-at-a-time analysis would understate, making global methods the more defensible default for this class of problem. Third, thermodynamic and life-cycle-assessment modelling uncertainty was shown, in this case study, to be a comparatively minor contributor to overall ranking uncertainty relative to the weighting of the SSbD pillars themselves — a finding that may or may not generalise to other technologies and should be tested explicitly rather than assumed in future applications. The complete workflow presented here — thermodynamic sub-model, indicator compilation, combination weighting, TOPSIS ranking, and the OAT/Sobol/Monte-Carlo/parameter-sweep sensitivity suite — is directly transferable to other SSbD case studies in renewable-energy hardware design, including heat-transfer fluids, battery electrolytes, and refrigerants for other thermal-energy-conversion technologies.

ACKNOWLEDGMENT

The authors gratefully acknowledge the open-access data and methodological resources made available by the European Commission Joint Research Centre, the National Renewable Energy Laboratory, and the International Geothermal Association, which underpin the case-study data compiled in Table 1.

CONFLICT OF INTERESTS

The authors confirm that there is no conflict of interest associated with this publication.

NOMENCLATURE

Symbol	Description	Unit
T_{evap}	Evaporator (heat-addition) saturation temperature	degC
T_{cond}	Condenser (heat-rejection) saturation temperature	degC
T_{crit}	Working-fluid critical temperature	degC
η_{carnot}	Carnot-limit thermal efficiency	-
η_{II}	Exergetic (second-law) efficiency	-
η_{th}	First-law (thermal) cycle efficiency	-
GWP100	100-year global warming potential	kg CO ₂ -eq/kg

ODP	Ozone depletion potential	-
x_{ij}	Raw value of indicator j for fluid i	-
$x_{ij}\text{-tilde}$	Vector-normalized value of indicator j for fluid i	-
w_j^{ent}	Shannon-entropy (objective) weight of indicator j	-
w_j^{sub}	Subjective (neutral dimension-level) weight of indicator j	-
w_j	Combined weight of indicator j	-
CC_i	TOPSIS closeness coefficient of fluid i	-
S_i, S_{Ti}	Sobol first-order and total-order sensitivity indices	-

REFERENCES

1. DiPippo, R. *Geothermal Power Plants: Principles, Applications, Case Studies and Environmental Impact*, 4th ed.; Butterworth-Heinemann/Elsevier: Oxford, UK, 2016.
2. National Renewable Energy Laboratory (NREL). Geothermal Resource Data, Tools, and Maps. Available online: <https://www.nrel.gov/gis/geothermal> (accessed on 29 May 2026).
3. Bao, J.; Zhao, L. A Review of Working Fluid and Expander Selections for Organic Rankine Cycle. *Renewable and Sustainable Energy Reviews* 2013, 24, 325-342.
4. Sala, S.; Caldeira, C.; Farcas, R.; Garmendia Aguirre, I.; Mancini, L.; Tosches, D.; Amelio, A.; Rasmussen, K.; Rauscher, H.; Riego Sintes, J. *Safe and Sustainable by Design Chemicals and Materials -- Framework for the Definition of Criteria and Evaluation Procedure for Chemicals and Materials*; EUR 31100 EN, JRC128591; Publications Office of the European Union: Luxembourg, 2022. <https://doi.org/10.2760/487955>.
5. European Commission, Joint Research Centre. *Safe and Sustainable by Design Chemicals and Materials -- Application of the SSbD Framework to Case Studies*; JRC131878; Publications Office of the European Union: Luxembourg, 2023.
6. Zhang, L.; Wang, L.; Sun, X.; Xia, L.; Tao, S.; Xiang, S.; Jin, S. Multi-Objective Evaluation Strategy Based on Data Envelopment Analysis for Working Fluid Selection in the Organic Rankine Cycle. *Processes* 2025, 13, 1013.
7. Andreasen, J.G.; Larsen, U.; Knudsen, T.; Pierobon, L.; Haglind, F. Selection and Optimization of Pure and Mixed Working Fluids for Low Grade Heat Utilization Using Organic Rankine Cycles. *Energy* 2014, 73, 204-213.
8. DiPippo, R. Second Law Assessment of Binary Plants Generating Power from Low-Temperature Geothermal Fluids. *Geothermics* 2004, 33(5), 565-586.
9. Heberle, F.; Schiffelechner, C.; Bruggemann, D. Life Cycle Assessment of Organic Rankine Cycles for Geothermal Power Generation Considering Low-GWP Working Fluids. *Geothermics* 2016, 64, 392-400.
10. National Renewable Energy Laboratory (NREL). *Systematic Review of Life Cycle Greenhouse Gas Emissions from Geothermal Electricity*; Technical Report NREL/TP-6A20-68474; NREL: Golden, CO, USA, 2017.
11. Hwang, C.L.; Yoon, K. *Multiple Attribute Decision Making: Methods and Applications, A State-of-the-Art Survey*; Lecture Notes in Economics and Mathematical Systems, Vol. 186; Springer-Verlag: Berlin, Germany, 1981.

12. Zou, Z.; Yun, Y.; Sun, J. Entropy Method for Determination of Weight of Evaluating Indicators in Fuzzy Synthetic Evaluation for Water Quality Assessment. *Journal of Environmental Sciences* 2006, 18(5), 1020-1023.
13. Saltelli, A.; Ratto, M.; Andres, T.; Campolongo, F.; Cariboni, J.; Gatelli, D.; Saisana, M.; Tarantola, S. *Global Sensitivity Analysis: The Primer*; John Wiley and Sons: Chichester, UK, 2008.
14. Jansen, M.J.W. Analysis of Variance Designs for Model Output. *Computer Physics Communications* 1999, 117(1-2), 35-43.
15. Sobol, I.M. Global Sensitivity Indices for Nonlinear Mathematical Models and Their Monte Carlo Estimates. *Mathematics and Computers in Simulation* 2001, 55(1-3), 271-280.
16. Kotas, T.J. *The Exergy Method of Thermal Plant Analysis*; Butterworths: London, UK, 1985.
17. ASHRAE. *ANSI/ASHRAE Standard 34-2019, Designation and Safety Classification of Refrigerants*; American Society of Heating, Refrigerating and Air-Conditioning Engineers: Atlanta, GA, USA, 2019.
18. Myhre, G.; Shindell, D.; Bréon, F.-M.; Collins, W.; Fuglestedt, J.; Huang, J.; Koch, D.; Lamarque, J.-F.; Lee, D.; Mendoza, B.; et al. Anthropogenic and Natural Radiative Forcing. In *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*; Stocker, T.F., et al., Eds.; Cambridge University Press: Cambridge, UK, 2013; pp. 659-740.