# A Multi-Criteria Framework for Zeotropic Mixture Selection: Performance Assessment and Composition Shift Analysis

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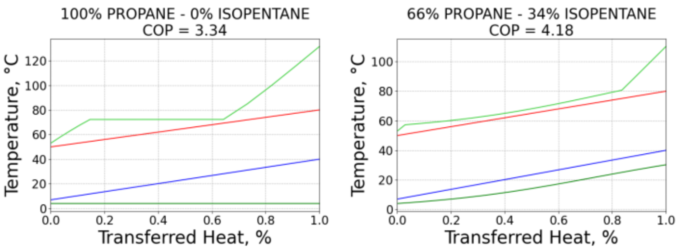
## 1. Introduction

- Constant-temperature phase change of pure refrigerants often leads to poor temperature matching and exergy losses[1].
- Zeotropic mixtures exhibit **temperature glide** during phase change caused by changing liquid and vapor compositions, enabling improved thermal matching and reduced irreversibilities.
- Oil circulation and fractionation can shift the circulating composition, introducing uncertainty around the nominal mixture ratio and affecting performance.




## 2. Research Objective

To develop a multi-stage screening framework that identifies zeotropic mixtures offering robust performance improvements across multiple operating scenarios, rather than optimizing mixtures for a single, case-specific application.

## 3. Screening Framework

**Stage I – Exploratory Screening:**
Identification of trends in performance improvement

$$COP = \frac{\dot{Q}_{sink}}{\dot{W}_c}$$

**Stage II - Refinement Screening:**
Application of engineering limits and exergy analysis with introduction of glide matching metrics

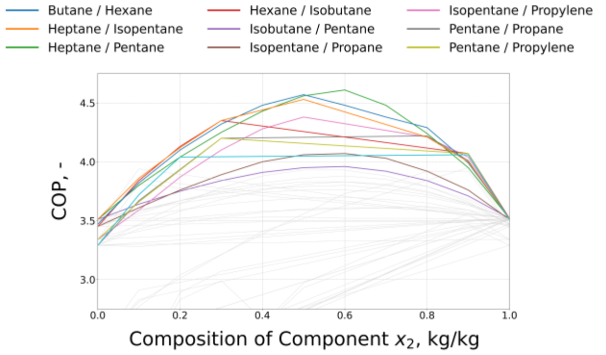
$$\pi_{glide} = \frac{\dot{E}_{D,component}}{\dot{E}_{D,pinch}}$$

**Stage III – Validation Screening:**
Analysis of mixture performance across five operating scenarios and definition of robustness criteria for final selection

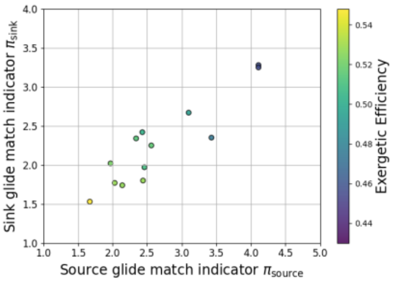
$$COP_{avg} = \frac{\sum_{i=1}^{N}(COP_i \cdot h_i)}{\sum_{i=1}^{N} h_i}$$

## 4. Performance improvements

- Hydrocarbon mixtures achieved COP **improvements of roughly 10–25%** compared to their pure-fluid counterparts, while maintaining acceptable pressures and discharge temperatures across all operating cases.




- Mixtures with good **glide match indicators**[2], especially on the heat source side, significantly reduce avoidable exergy destruction, explaining the higher COP.

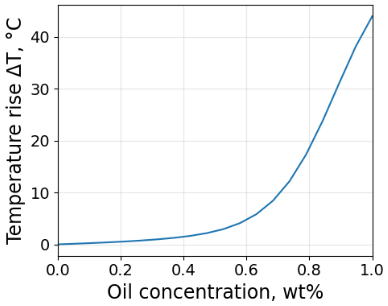



## 5. Oil Solubility Differences

- The presence of oil in the refrigerants mixture alters the phase equilibrium, which is described as a non-ideal multicomponent system:

$$\phi_{r,i} y_{r,i} P = \gamma_{r,i} x_{r,i} f_{r,i}^{0}$$

- At constant pressure, the saturation temperature in the presence of oil is higher than that of the oil-free single fluid refrigerant or refrigerant blend[3].



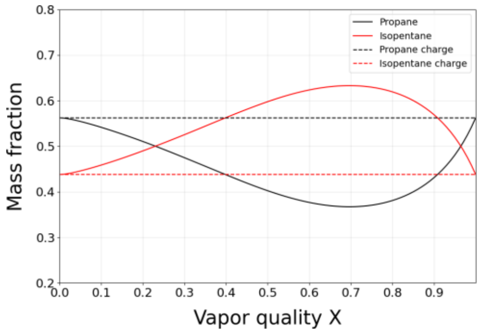

- Differences in oil solubility between mixture components can create absorption of one component into the oil which results in composition shift.

## 6. Slip Effects

- The composition during phase change may deviate from the charged composition as a consequence of **liquid hold-up**. The composition shift is expressed as[4]:

$$\delta = C_{j,i} - D_{j,i} = \frac{X_j(1 - X_j)(S_j - 1)(x_{j,i} - y_{j,i})}{(1 - X_j)S_j + X_j}$$

- As vapor quality increases, preferential evaporation leads to enrichment of the circulating fluid in the low-boiling component, causing a deviation from the nominal charged composition.




## 7. Conclusion

- Systematic screening of mixtures across a range of pressures and temperatures, is required to ensure robust performance improvements.
- The combined effects of oil solubility and liquid holdup introduce uncertainty in the circulating mixture composition, which cannot be captured by nominal charge specifications alone.

## 8. Acknowledgments

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## 9. References

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[2]Zühlsdorf, B., Jensen, J. K., Cignitti, S., Madsen, C., & Elmegaard, B. (2018). Analysis of temperature glide matching of heat pumps with zeotropic working fluid mixtures for different temperature glides. *Energy*, *153*, 650-660.

[3]Fleming, J. S., & Yan, Y. (2003). The prediction of vapour–liquid equilibrium behaviour of HFC blend–oil mixtures from commonly available data. *International journal of refrigeration*, *26*(3), 266-274.

[4]Zhao, L., & Bao, J. (2014). The influence of composition shift on organic Rankine cycle (ORC) with zeotropic mixtures. *Energy conversion and Management*, *83*, 203-211.