Refrigerant Column

Kyla & Värme, No. 6, June 2024

Can Hydrocarbon Blends Be a Future Refrigerant Option?

By Björn Palm

Background

About 30 years ago, there was much discussion at scientific conferences on the advantages and disadvantages of using **refrigerant blends** instead of pure substances. At that time, the industry was looking for replacements for CFCs and HCFCs that could be used without system modifications—that is, refrigerants with vapor pressure curves similar to the phased-out substances.

Since blends often had a **temperature glide**, the question was raised whether this could actually be an advantage in some applications.

Today, with the phase-out of high-GWP refrigerants, many new blends are again being proposed. The chemical industry's goal is to create refrigerants with:

- **Low GWP**
- **Low flammability**
- Vapor pressures similar to existing refrigerants

The Challenge: Low GWP vs. Low Flammability

There is a fundamental **conflict** between low GWP and low flammability.

- **Low flammability** is associated with **stable molecules**.
- **Low GWP** requires **unstable molecules** that are quickly broken down by natural processes.

Thus, it is difficult to find a non-flammable refrigerant with a low GWP. One possible solution is to **blend** stable, higher-GWP substances with unstable, low-GWP ones. Flammability can also be reduced by **adding CO_2**.

Given the almost infinite number of possible combinations, it is clear why there is strong interest in developing blends with the desired combination of **low GWP, low flammability, and suitable pressure levels**.

Zeotropic and Azeotropic Blends

Blends can be of two types:

- **Azeotropic:** Vapor composition is identical to the liquid composition during boiling. The mixture has a **single boiling point** and behaves like a pure refrigerant—**no glide**.
- **Zeotropic:** The more volatile component evaporates faster, leaving behind the less volatile one. The mixture exhibits **glide**, i.e. a temperature range between bubble point and dew point. Depending on the components, glide can be less than 1 K or greater than 20 K.

Glide as an Advantage

A key argument for blends is that their glide can be **matched** to the temperature change of the heat source and sink in a heat pump or refrigeration system.

In theory, this reduces **thermodynamic losses** and improves COP.

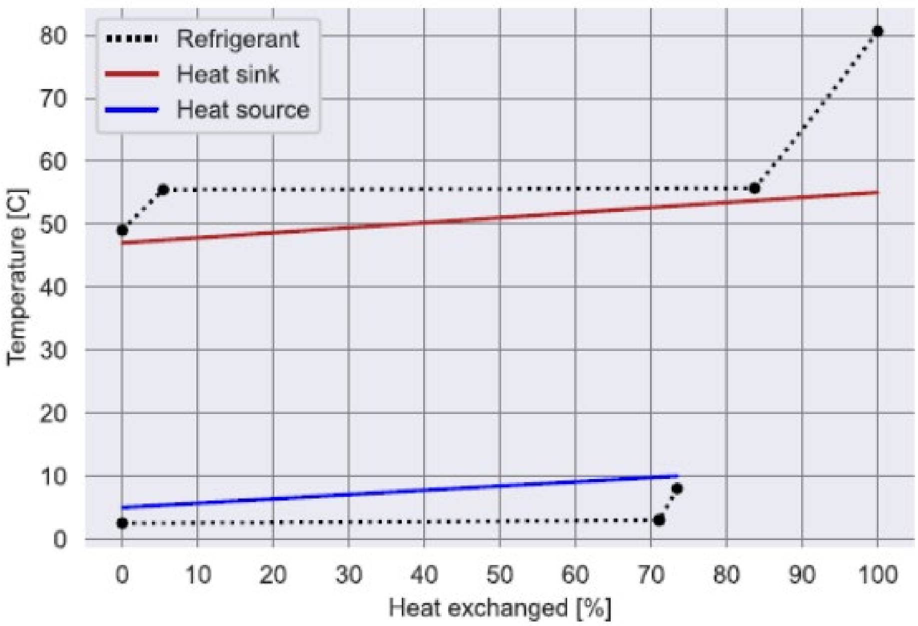


Figure 1. Temperature profiles in evaporator and condenser for a pure refrigerant. From [1].

However, this advantage depends on **counter-flow** heat exchange. With **cross-flow** (e.g., finned coils), exploiting glide is much more difficult.

Moreover, systems require **superheat** at the evaporator outlet. With matched glide, achieving sufficient superheat requires **larger heat exchanger surfaces**, lowering the evaporation temperature.

Practical Limitations of Blends

There are several drawbacks with blends:

- **Worse transport properties** (thermal conductivity, viscosity) than expected from interpolation.
- **Reduced heat transfer** due to **mass transfer resistance**: the more volatile component evaporates faster, creating concentration gradients and diffusion resistance.
- **Composition shifts**:
  - If the system leaks, the remaining refrigerant composition changes.
  - Topping up does not restore the original mix.
  - Different flow rates of vapor and liquid can also cause composition differences in the system.

New Research on Natural Blends

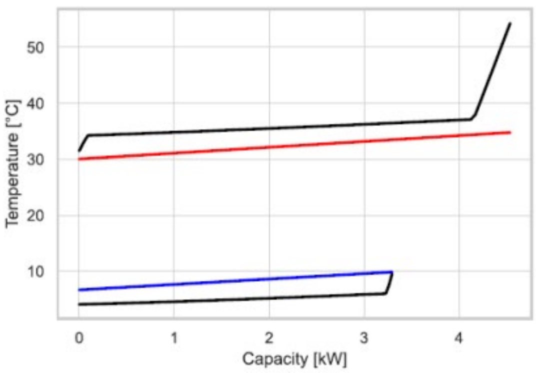
Several theoretical studies have shown potential benefits of blends with matched glide, but often without accounting for the drawbacks above.

In **August 2023**, *Matteo Caramaschi* defended his doctoral thesis at the Technical University of Denmark. Across several papers, he studied blends of **natural refrigerants** using both theoretical models and experiments.

The tested blends included:

- Propane/CO_2
- Propylene/CO_2
- Dimethyl ether (DME)/CO_2
- Propylene/DME

CO_2 concentrations were always low (≤ 5%). Glide ranged between 2.5 and 8.3 K. The heat-source and sink temperature differences varied from **very small** (evaporator 10/7 °C, condenser 30/35 °C) to **very large** (30/15 – 40/55 °C).



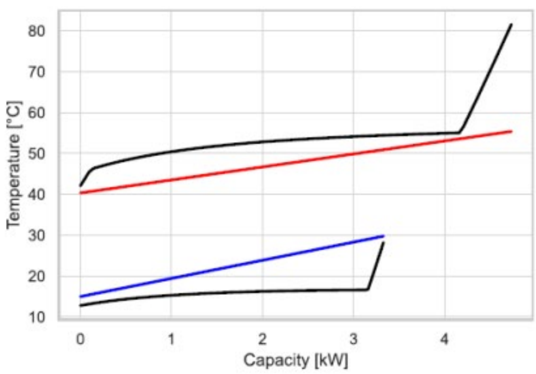


Figure 2. Temperature profiles in evaporator and condenser for two cases with low vs. high temperature difference. Left: Propylene/DME. Right: DME/CO_2. From [1].

In both cases, refrigerant temperatures (black) followed the heat carrier temperatures closely due to glide. In the low-glide case, superheat was small, and the temperature difference in the evaporator was low—without glide, the required superheat would have been easier to obtain.

Findings

The experimental results showed that:

- **At small temperature differences**: the COP gain with blends is **minimal**.
- **At large temperature differences**: blends provided **significant COP improvement**.

The thesis also demonstrated excellent COP results for **DME** and some of its blends—suggesting DME may be an **overlooked refrigerant** worth revisiting.

Conclusion

Hydrocarbon blends are not without challenges—poorer transport properties, composition shifts, and reduced heat transfer remain obstacles.

But research indicates that in **specific applications with large source/sink temperature differences**, blends can deliver real performance benefits.

The promising results with **DME and blends** highlight that natural refrigerant mixtures may play a role in future system designs.

Reference:
[1] Caramaschi, M. 2024. *Experimental investigations and modeling of natural refrigerants in low-charge heat pumps*. PhD thesis, Technical University of Denmark.
