Glide matching with binary and ternary zeotropic* refrigerant mixtures
Part 1. An experimental study

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An improvement of the coefficient of performance (COP) of the refrigeration cycle can be realized when temperature profiles of the refrigerant mixture and the heat transfer fluid (HTF) are matched. For the same temperature lift, the benefit of glide matching increases as the application glide increases. High-glide binary mixtures composed of components far apart in boiling points tend to have a non-linear relationship between temperature and enthalpy in the two-phase region. The introduction of an intermediate boiler as a third component can linearize this relationship and, theoretically, increase the cycle COP when heat-source and heat-sink fluids are substantially linear (e.g. water, brines, dry air). The research described in this paper was directed at exemplifying this characteristic of ternary mixtures by experimental evaluation of the performance of an R23/142b binary mixture and an R23/22/142b ternary mixture in a generic laboratory breadboard refrigeration system.
(Keywords: zeotropic mixtures; Lorenz cycle; refrigeration; heat pumping; refrigerant mixtures; non-linearity)

Correspondances de glissements avec les mélanges frigorigènes zéotropes binaires et ternaires
1ère partie: Étude expérimentale

On peut améliorer le coefficient de performance (COP) du cycle frigorifique quand les profils des températures du mélange frigorigène et du fluide caloporteur (HTF) sont identiques. Pour le même relevage de température, les correspondances de glissements augmentent parallèlement au glissement lui-même. Le rapport entre température et enthalpie dans les zones biphasiques serait plutôt non-linéaire pour les mélanges binaires très glissants, formés de composants dont les points d'ébullition sont très éloignés. L'introduction d'un générateur intermédiaire comme troisième composant peut linéariser ce rapport et, en théorie, augmenter le COP du cycle quand les fluides sources de chaleur et sources de froid sont très linéaires (par ex., l'eau, les liquides à bas point de congélation, l'air sec). Les recherches décrites dans cet article ont servi à illustrer cette caractéristique des mélanges ternaires en évaluant la performance du mélange binaire R23/142b et du mélange ternaire R23/22/142b dans un système frigorifique expérimental.
(Mots clés: mélanges zéotropes; cycle Lorenz; froid; pompe à chaleur; mélanges frigorigènes; non-linéarité)

In theory, the use of zeotropic mixtures can result in an improvement in the cycle coefficient of performance (COP) when the temperature profile of the evaporating and condensing mixture matches that of heat-source and heat-sink fluids in the counter-flow evaporator and condenser. The benefits are derived from reducing the irreversibilities in the heat exchangers.

The concept of glide matching is presented in Figure 1 where Carnot and Lorenz cycles are shown working at the same temperature profiles of the heat transfer fluid (HTF). The shaded areas in the figure are approximations of the heat transfer irreversibilities. For the Carnot cycle, even infinite heat exchangers cannot eliminate the irreversibilities if a sensible HTF is used, as is shown in the figure. However, for the Lorenz cycle, increase in the heat transfer area will cause decrease in heat transfer irreversibilities. (Note that the temperature profile of the HTF is shown in Figure 1 to provide a reference for outlining the two thermodynamic cycles, and not to indicate HTF's entropy change in the evaporator and condenser; transfer of heat at a finite temperature difference causes unequal entropy changes of the heat-exchanging fluids.) Sensible fluids such as water, brines and air without condensation occurring exhibit nearly constant specific heats over the temperature range experienced in the heat exchanger, which results in a nearly linear temperature profile during heat exchange. Unfortunately, the temperature of high-glide zerotropic mixtures generally does not change linearly as a function of enthalpy (or of entropy, which is nearly the same physical requirement). This results in non-linear refrigerator profiles with the potential to 'pinch' with the sensible fluid, as illustrated in Figure 2.

* The word 'zeotropic' is used to describe a refrigerant mixture which changes (tropic) in boiling (zeo) behaviour, in lieu of the double negative prefixed non-zeotropic.

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Figure 1 Efficiency advantage of the Lorenz cycle
Figure 1 *Rendement du cycle* Lorenz

Figure 2 Inefficiencies resulting from two-phase non-linearity
Figure 2 *Inefficacité due à la non-linéarité biphaseque*

An approach to visualize the correcting of this two-phase non-linearity via third component is shown in Figure 3. Here, each component of a mixture is shown as an area of height equal to its boiling point and of length equal to its total enthalpy (mass fraction times specific enthalpy). The top figure represents a binary where the predominant thermal component is the more volatile one (i.e. lower boiling point). This results in a concave profile because considerable evaporation must occur before the influence of the less volatile component is felt.

The middle figure represents the opposite case where the less volatile component is felt rather early in the evaporation process and so the binary's saturation temperature begins changing significantly at very low qualities and convex profiles result. We conjectured that by adding a fluid of intermediate boiling point, the temperature profile might be linearized. It is this concept this study attempted to verify, and so the binary and ternary components and compositions were selected purely on the basis of their normal boiling points. The magnitude and non-linearity of the temperature glide will tend to increase as the extreme components are selected with more widely diverging boiling points. Introduction of a fluid with an intermediate boiling temperature will tend to even out the rate of change of the temperature-enthalpy curve.

**Test apparatus and test procedure**

The tests were conducted on a breadboard heat pump apparatus which was constructed for a previous study and is described in detail in reference 1. In essence, the system works as a counter-flow, water-to-water heat pump.

The evaporator was composed of two 6.1 m (20 ft) sections, each bent into a hairpin shape for compactness, connected in series. The sections are extrusions with an integrally finned centre passage surrounded by rectangular passages. In the tested configuration, evaporating refrigerant flowed through the centre passages and heat source water through the surrounding rectangular passages. Hard copper tubes were attached over the four hairpin legs to create a third concentric passage used (in some of the tests) for heat exchange between refrigerant leaving the condenser and the heat source water throughout the length of the evaporator. Thermocouples were spaced at 2 ft (0.61 m) intervals inside 10 ft (3.05 m) long wells which were inserted into the evaporating refrigerant centre passages of each hairpin leg. The heat-source water temperature was measured in wells at the inlet and outlet, and by surface thermocouples at the cross-over between each 10 ft section. Temperature profiles measured by these thermocouples are presented in Figure 6.

The system employed a positive displacement, suction-vapour-cooled, open compressor driven by a variable-speed motor through a shaft dynamometer. The expansion device was operated manually. The design of the condenser did not allow placing thermocouples inside the heat exchanger; only inlet and outlet refrigerant and HTF temperatures were measured.

The evaporator capacity was measured by a calorimeter method with the enthalpy method on the evaporator-water side as a secondary measurement. The water flow was measured by a turbine meter and by comparing the temperature change of the water across the metered electric heaters used to load the evaporator. Analogous methods to the secondary evaporator capacity measurement methods were applied to the condensing water loop to measure the condenser capacity.

All tests were performed with evaporator water entering and leaving temperatures of 26.7 °C (80 °F) and 12.8 °C (55 °F), respectively, and condenser entering and leaving water temperatures of 27.8 °C (82 °F) and 47.2 °C (117 °F).
The evaporator exit close-to-saturation condition was
maintained by two accumulators installed in series. A
conventional accumulator with an oil return J tube
was located directly in front of the compressor and was
used to protect the compressor on start-up. This
accumulator was valved off and bypassed during steady-state
operation at which time it would store excess refrigerant
in the system. Another accumulator was located at the
evaporator outlet and was used to establish a consistent
state of slightly misty vapour leaving the evaporator
as a test criterion and to reduce sensitivity to
refrigerant charge. This system design ensured that only vapour
with a slight mist carry-over could leave, establishing
the evaporator exit condition as near saturation.

Subcooling was controlled with a manually operated
expansion valve. In previous tests on this apparatus,
subcooling was adjusted to be as near saturation as
possible but still subcooled. This criterion was
somewhat unfair to pure refrigerants and to undergliding
zeotropic mixtures. Their COP can be increased by
subcooling to as near the inlet water temperature as
possible without pinching. Therefore, this series of tests
was performed with two subcooling criteria: first, that
the liquid line sight glass was clear; and, second, that the
temperature of the refrigerant leaving the condenser was
near that of the inlet water (27.8 °C (82 °F)). In practice
this temperature ranged from 28 °C (82.4 °F) to 33.1 °C
(91.5 °F). Exceptions to this criterion were several tests in
which the effect of heat transfer between the liquid line
and the evaporator was studied; in these tests, in which the
refrigerant appeared to be non-linearly pinching at
the condenser outlet, the expansion valve was opened to
allow two-phase refrigerant leaving the condenser.

Because the coefficient of performance of vapour
compression systems is sensitive to heat exchanger size
per unit capacity, and the heat exchanger size was fixed,
it was desired to run tests at constant evaporator capacity
using the variable-speed compressor drive to compensate
for the variations in capacity inherent in the different
refrigerants to be tested. This criterion was compromised by
the need to avoid the 600–800 rev min⁻¹ band in
which high system vibrations and unduly reduced
efficiency were observed. In practice, measured evaporator
capacities range from 3.119 kW (10730 Btu h⁻¹) to
4.457 kW (15330 Btu h⁻¹) with the exception of test
21, which was performed at 5.777 kW (19870 Btu h⁻¹).
The very large size of the heat exchangers (resulting in
approximately 2.8 °C (5 °F) average effective temperature
difference and R22 pinching at approximately 1/4 the
evaporator length) somewhat reduced sensitivity to this
heat exchanger size criterion.

Refrigerant composition was determined by gas
chromatographic analysis of samples taken from the
compressor discharge line at the beginning and end of
each test. The composition would change from test to
test for the same initial charge as a result of differing
amounts of refrigerant being held in the separating
accumulator at the evaporator outlet, which would
selectively store the less volatile mixture components.

Test plan

The binary mixture chosen for this study was one of R23
(trifluoromethane) and R142b (chlorodifluoroethane).
These refrigerants are quite far apart in their normal
boiling points, 82.1 °C (144.8 °F) and −9.8 °C
(14.4 °F), respectively, suggesting that their mixture
would tend to have a high temperature glide and a
significant temperature–enthalpy or temperature–
temperature–entropy non-linearity in the two-phase region.
The intermediate boiler chosen for demonstration of linearization
by addition of a third component was R22
(chlorodifluoromethane) characterized by a normal
boiling point of −40.8 °C (−41 °F).

The tests were planned to indicate the best-performing
compositions of the R23/142b and R23/22/142b mixtures
with the constraint not to exceed the operating pressure
of R22. The best COP was expected to occur near the
point of glide matching to the heat-source fluid, i.e. at a
13.9 °C (25 °F) glide. For the binary mixture, the best
performance could be found by stepping the composition
from one pure component to the other in equal intervals
with extra points taken in areas of rapid performance
change and near efficiency peaks. The extra degree of
freedom provided by ternary mixtures required more
thought as to appropriate test compositions.

A two-phase temperature glide diagram for the studied
ternary, R23/22/142b, proved to be helpful in planning
the experiment. Such a diagram is shown in Figure 4,
where the temperature glide for the mixture is mapped in
24 mass-fraction steps with +/− non-linearities noted
pithetically and R22 isobar superimposed. The
positive and negative non-linearity numbers indicate the
maximum and minimum that the mixture temperature
exceeds that of a hypothetical linear fluid (i.e. ideal
mixture) on a temperature–enthalpy diagram, where
both fluids are compared at the same quality point and
have the same bubble and dew point properties. The R22
isobar indicates those compositions which have a bubble
pressure equal to the saturation pressure of R22 at a
bubble temperature of 0 °C. The diagram was developed
using the thermodynamic properties routines
implementing the Carnahan–Starling–DeSantis equation of
state, taken from the REFPROP package.

First, it can be observed in Figure 4 that, as expected,
the binary mixture of the components farthest apart in
boiling points, R23/142b, shows the greatest non-
linearity. This binary mixture has two points of a 13.9 °C
(25 °F) glide, one of them occurring below the R22 isobar.
Thus, the first part of the test plan was to perform tests
with the binary mixture R23/142b starting with pure

![Figure 4](https://example.com/figure4.png)

**Figure 4** Temperature glide (°C) at Tboil = 0°C for the mixture
R23/22/142b.

![Figure 4](https://example.com/figure4.png)

**Figure 4** Glissement des températures à Tboil = 0°C pour le mélange
R23/22/142b.
R142b until either efficiency began to drop off excessively or the R22 isobar was exceeded.

Also from Figure 4, we can observe that the best ternary linearity with a 13.9°C (25°F) glide occurs near the R22/142b binary line at approximately 60% R22. Technically, it would be most interesting to reach this point by following either a constant pressure or constant glide line from the R23/142b binary line. In practice, following such a line would be exceedingly difficult, and the decision was made to follow the easier test path of moving upward from approximately 50%/50% R22/142b in small increments of R23.

As a comment on the increased flexibility with ternary mixtures, one can follow the 13.9°C (25°F) constant-glide line from the R23/142b binary line and observe that this glide may be achieved in the ternary region over a broad and continuously varying range of pressures, much of which is below the R22 isobar. In contrast, if one were restricted to binary combinations, there would be none with this glide using R22/142b, two with R23/142b (but only one below the R22 isobar) and two with R23/22 (both above the R22 isobar). The two binary 13.9°C (25°F) glide points near the R23 apex would be expected to be critical or near critical in the condenser.

Test results and discussion

The primary goal of this project was to demonstrate improvement of two-phase linearity by the use of ternary mixtures. Hence, primary data analysis is to be directed at comparing evaporator temperature profiles; condenser instrumentation was inadequate to allow similar analysis of that heat exchanger. This said, the motivation for linearizing temperature glide is that it, theoretically, will improve efficiency. Therefore, it is useful to use an efficiency plot as a framework for analysis of test results.

The operating conditions of the performed tests and a summary of the test results are given in Table 1 of this paper. The coefficient of performance is presented as a function of evaporator refrigerant temperature glide in Figure 5. The pure refrigerants R22 and R142b are shown at the zero glide ordinate as tests 1 and 2. Pure R23 could not be tested because it is super-critical at room temperature. The difference in COP shown for the two pure refrigerants emphasizes the point that glide matching is not the only refrigerant property that affects cycle efficiency. It has previously been observed that, on this apparatus, lower volumetric capacity refrigerants such as R142b tend to show reduced COP as a result of compressor mechanical losses becoming a greater proportion of total capacity. Individual refrigerant properties can also affect other efficiency-related areas.

![Figure 5](https://via.placeholder.com/150)

**Figure 5** Coefficient of performance as a function of evaporator temperature glide

**Table 1** Measured data

<table>
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<th>Temperatures in condenser</th>
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such as pressure drops and heat transfer coefficients. Throughout this discussion it must be remembered that every mixture test is performed with a different refrigerant. Effects due to glide matching versus other property changes can never be completely separated in an experimental study.

Referring to Figure 5, adding R23 to R142b improved the COP by 28% without and 33% with heat exchange between the liquid line and evaporator (tests 5 and 10 versus test 2). Adding R142b to R22 resulted in a 22% improvement in COP that did not show sensitivity to heat exchanger use (tests 12 and 13 versus test 1). Addition of R23 to the binary mixture R22/142b resulted in ternary COPs as much as 28% better than that of pure R22 (test 22 versus test 1). This peak COP matches that previously reported for the binary mixture R22/114. The COP improvement reported by Mulroy et al. was slightly higher (32% versus 28% above) because subcooking was not employed for undergliding refrigerants in that test series. Use of the liquid-line/evaporator heat exchanger appears to slightly improve the COP for both the ternary mixture and the R23/142b binary mixture.

One interesting observation that can be made from Figure 5 is that a small amount of R23 seems to hurt performance, probably due to its low critical point. Tests 3 and 4, in which a small amount of R23 has been added to pure R142b, show lower efficiency than test 2 performed with pure R142b. With higher amounts of R23 efficiency improves as the benefits of glide matching are felt.

Before discussing experimental temperature profiles, it is useful to briefly discuss how water and refrigerant temperature profiles that are matching and linear against an entropy abscissa would appear when plotted against enthalpy and distance. Translation to an enthalpy axis would result in a small alteration, because entropy change is substantially enthalpy change divided by the absolute temperature, which exhibits a very small percentage change throughout the evaporator. Since a counter-flow evaporator was used and the water and refrigerant travelled the same distance during the heat exchange, the temperature points will map directly over one another when going to a distance scale. Temperature profiles on the distance scale for tests 6, 12, 17 and 22 are shown in Figure 6.

On an enthalpy–distance coordinate diagram, the distance scale will distort the water temperature profile in accordance with the heat transfer equation, $q = UA \Delta T$, in which distance is proportional to $A$ and $U$ varies primarily with refrigerant quality and heat flux. No matter what the shape of the water temperature profile on the temperature–distance scale, going backwards will, by properties, map back to a straight line on a temperature–enthalpy diagram. If the refrigerant temperature–enthalpy profile is linear and matching that of water, it will appear on a temperature–distance scale as displaying a constant refrigerant-to-water temperature difference. The exercise of mapping temperature–distance plots to an abscissa that will give a linear water temperature profile (effectively mapping to temperature–enthalpy) has been carried out for the selected tests in Figure 7, the abscissa of which has been dubbed pseudo-enthalpy. It is scaled in terms of equal enthalpy units (i.e. mass flow x specific enthalpy change).

Tests 6 and 17 are good choices for comparing non-linear with linear profiles in that their glides are nearly equal: 11.8°C (21.2°F) and 11.6°C (20.8°F), respectively, approximately matching the evaporator–water glide of 13.9°C (25°F).

For ternary test 17 (R23/22/142b (2.5/48.6/48.9)), the mixture glide can be seen to be nearly linear and matching, as evidenced by a nearly uniform temperature difference between the refrigerant and water in Figure 6 and a linear refrigerant temperature profile in Figure 7. The concave shape of the two curves in Figure 6 is the result of greater heat transfer and hence greater water cooling on the right-hand side (water inlet and refrigerant outlet) of the curve resulting from the greater refrigerant-side heat transfer coefficient at high qualities, and the greater average refrigerant-to-water temperature difference resulting from this mixture being slightly undergliding.

The temperature plots for binary test 6 (R23/142b

![Figure 6](image)

Figure 6 Evaporator temperature profiles on the distance scale for selected tests
Figure 6 Profils des températures de l'évaporateur sur un intervalle déterminé pour des essais spécifiques

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Figure 7  Evaporator temperature profiles remapped to force a linear temperature profile for the sensible heat transfer fluid.

Figure 7  Profils des températures de l'évaporateur redessinés pour arriver à un profil des température linéaire des fluides caloporteurs sensibles.

(7.9/92.1)) show a strong pinch point resulting from non-linearity for much of the midsection of the evaporator. Glide matching benefits cease once a coil begins to pinch. The only efficiency benefits expected from adding R23 are due to glide matching. Otherwise R23 addition would lower the COP due to its low critical temperature. Therefore, peak efficiency for R23/142b would be expected to occur with less R23 at a point where pinching has not yet occurred, as can be seen to be the case in Figure 6. Comparing with test 17, we have seen a demonstration that addition of the intermediate boiler, R22, will improve the linearity of the mixture R23/142b.

For the other binary mixture tested, R22/142b (57.7/42.3), test 12, the gradually increasing refrigerant–water temperature difference with pinching at the refrigerant inlet side indicates that linearity might be good (as can be seen to be the case in Figure 7), but that the temperature glide is much too small. The glide shown is nearly the highest possible with this binary mixture: hence this composition was chosen to constitute the base binary mixture to which R23 was added for ternary tests. Further tests demonstrated that, given a binary mixture of good linearity but insufficient glide, the glide may be increased without losing linearity by adding a third component outside the normal boiling point interval of the original constituents.

The final temperature profiles to be considered are those of the highest efficiency test, test 22 (R23/22/142b (2.3/50.6/47.1)). This ternary profile shows good linearity and glide matching. The liquid-line/evaporator heat exchanger used for this test results in a lower entry quality and, consequently, a less smooth curve than would be shown by the same mixture without such heat exchange. The benefit of this heat exchanger results from changed operating pressures and does not show in a temperature profile plot.

Conclusions

The two-phase, temperature–entropy linearity of a binary mixture was shown to be improved by the introduction of a third component of intermediate normal boiling point. Generally speaking, the greater the difference in the normal boiling points of a binary’s components the larger the temperature glide will be and the more non-linear the mixture temperature profile will be. However, it was demonstrated that the magnitude of the two-phase temperature glide of a linear binary mixture was increased without loss of linearity by addition of a third component outside the normal boiling point range of the original constituents.

The flexibility of ternary mixtures to provide a desired two-phase temperature glide over a broad range of component compositions and operating pressures was demonstrated.

The use of the liquid-line/evaporator heat exchange was shown to improve cycle COP for the refrigerant mixtures tested. With the combined effects of the glide matching and liquid-line/evaporator heat exchange, a 28% better COP was measured than that of pure R22.

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