A proposal for a non-flammable, fluorine-free, CO_2-based mixture as a low TEWI refrigerant

Proposition d'un mélange ininflammable, non-fluoré et à base de CO_2 comme frigorigène à faible TEWI

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ABSTRACT

A thermodynamic analysis of a simple inverse cycle is proposed as a means to evaluate mixtures of CO_2 and four organic substances (propane, iso-butane, dimethyl-ether and propylene) as working fluids. The cycle features an internal heat exchanger and is designed to cool down a finite heat capacity flow on the cold side. The analysis covers trans-critical as well as sub-critical cycles. For each organic substance, the composition is optimized. Flammability is accounted for. Dimethyl-ether (DME) turns out to be the best option, as a relatively low mass fraction of this compound is sufficient for reaching the thermodynamic optimum. In this way, a simple, sub-critical refrigeration system may be obtained featuring a non-flammable working fluid and a significant COP increase with respect to pure CO_2.

1. Introduction

CO_2 refrigeration systems are experiencing an increasing market share in some applications. For example, in Europe, trans-critical CO_2 systems have surpassed a 14% market share in the food retail sector (Dilshad et al., 2020). This success is due to the huge effort done by researchers from academia and the industry to increase the efficiency of these systems (Gullo et al., 2018). New attempts are done to extend this success to other sectors, e.g. transport refrigeration (Minetto et al., 2023). However, the improvements are often done at the expense of an increasing complication of the refrigeration system, e.g. the use of multiple ejectors (Gullo et al., 2018b).

An alternative path towards the improvement of CO_2-based systems could be sought through the use of fluid mixtures. This approach would allow performance improvements comparable to those obtained with complex cycles, as shown recently by Sànchez et al. (2023). This doesn't mean that blends would not be useful in more complex systems, as shown in Martinez-Ángeles et al. (2023), where a parallel compression system using a CO_2/R1233ze(E) mixture [90/10%] has been shown to bring a COP improvement of almost 12%.

Cycles employing mixtures, when compared to cycles using pure CO_2, will have the following features:

- higher critical temperature (in some cases leading to sub-critical operation)
- lower operating pressure
- lower volumetric refrigeration capacity
- variable evaporation temperature (glide)

The last feature (Lorentz cycle) may be useful whenever the heat source has a finite heat capacity, as in the case of water chillers or direct-expansion air conditioners. Even in the case of a refrigerated cell in a food storage plant, a well-measurable temperature difference exists between the inlet and outlet of the evaporator, air flow rate being limited. The glide-matching between the refrigerant mixture and cooled fluid has been pursued for CO_2/propane mixtures since the work of Kim et al. (2008).

1.1. Fluid selection

Many substances may be considered possible components in a CO_2-based mixture. In our previous work on this subject (Vaccaro et al., 2023), we have examined various fluid categories and we have shown

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Nomenclature

COP	Coefficient of performance
DME	Dimethyl-ether
ε	Heat exchanger efficiency
h	enthalpy [kJ/kg]
HFO	Hydro-fluoro-olefin
IHX	Internal heat exchanger
$\dot{m}$	Mass flow rate [kg/s]
Q	Vapour quality
$\dot{Q}$	Thermal power [kW]
T	Temperature [K]
x	CO_2 mass fraction

that, among selected fluids, the best results were obtained using a mixture of CO_2 and an HFO (R1234yf), as confirmed by Martinez-Ángeles et al. (2023).

In this second work on the same topic, we have decided to concentrate on fluorine-free substances. This decision is partially related to the recent trend to include HFOs among PFAS (Per Fluoro Alchil Substances), as e.g. in ECHA Restriction Report (2023).

Hence we have selected a relatively small set of refrigerants: propane, isobutane, dimethyl-ether and propylene. All these substances, when mixed with CO_2, give a performance improvement with respect to pure CO_2. However, all these substances are highly flammable. Therefore, an interesting issue is the flammability of the mixture. According to ISO 817 2014, refrigerants may be divided into 4 classes; 1) non-flammable, 2 L) mildly flammable, 2) flammable and 3) highly flammable. Given that distinction between 2 and 2L classes is bound to the flame propagation velocity, we cannot specify the mixtures in this respect, due to the lack of experimental data. Therefore, in this paper, we will classify the blends into only 3 classes.

If non-flammability or mild flammability is sought, CO_2 must be the main component of the mixture. However, sometimes even low quantities of a flammable substance may make the mixture highly flammable. Therefore, a dedicated analysis must be performed for each substance.

1.2. System configuration and modelling

As already stated, the use of a mixture may be seen as an alternative to cycle complications (e.g. expansion work recovery) in the effort for improving the performance of CO_2 refrigeration systems. Therefore, a simple refrigeration system, comprising a compressor, condenser (or gas cooler), internal heat exchanger (IHX) and evaporator, has been taken as a reference (Fig. 1). The system is constrained by the ambient temperature, that fixes the minimum temperature of the hot heat exchanger (point 3), and by a minimum superheating at the compressor inlet (point 1), to avoid liquid ingestion. The sub-cooling from point 3 to point 4 is obtained in the IHX, where heat is transferred from the hot liquid to the cold fluid exiting the evaporator at point 0. If the IHX does not exchange heat with the environment, it must be:

$$h_3 - h_4 = h_1 - h_0 \tag{1}$$

Note that point 0 can be well within the two-phase zone, being the superheating guaranteed by the IHX. This represents a departure from what was written in the previous paper by the same authors (Vaccaro et al., 2023), where a saturated state was imposed at the evaporator exit. In this way, we add a further degree of freedom to the system configuration, which may be very useful for the optimization of the evaporator. For a given mixture composition, moving point 0 to the left (i.e. reducing the vapour quality at the evaporator exit) reduces the glide. Therefore, a desired value of glide may be re-established by increasing the quantity of added fluid to the mixture. Within certain limits, this improves the COP, as will be shown later. Note also the increasing downward slope of the isotherms on the right side of the saturation zone, which makes the glide very sensitive to the position of point 0.

To show some quantitative results, a set of reference values have been fixed for the fundamental system parameters (Table 1). A system that produces chilled water at 7°C is taken as a reference, but the results apply to any other case that allows a performance improvement employing a variable evaporation temperature. The minimum temperature difference between the cooled fluid and the evaporator is 5°C.

Note that the values reported in Table 1 are specified only as a common base for the sake of comparison between the various mixtures, without any reference to an existing refrigeration system. The system size is not constrained, in order to keep the analysis as general as possible. The efficiency value assumed for the compressor must be

Table 1
Main variable assumptions for all assessed cycles.

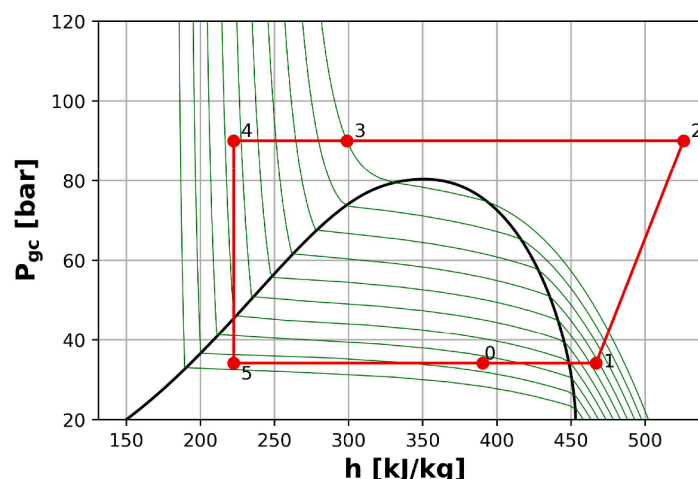| Parameter	Value
Gas cooler/condenser exit temperature	40°C
Compressor efficiency	0.8
IHX Heat exchanger efficiency	0.8
Pinch point temperature difference	5°C
Cooled fluid inlet temperature	12°C
Cooled fluid temperature drop	5°C
Minimum superheating at the compressor inlet	2°C

Fig. 1. Example of the cycle with IHX for a 95/5% CO_2/DME mixture.

revised once the size and degree of refinement of the case study are defined.

The thermodynamic cycle is modelled by imposing the energy balance for each component. Fluid properties are evaluated through NIST Refprop 10.0. The use of Refprop for mixtures may cause slight errors. A comparison between the experimental data published by Tsang and Street (1981) and the data calculated by Refprop has shown a maximum error on the predicted mole fraction below 5%.

The efficiency of the IHX is defined as:

$$\varepsilon = \frac{\dot{Q}}{\min\left(\dot{Q}_{\max\_34}, \dot{Q}_{\max\_01}\right)} \qquad (2)$$

where

$$\dot{Q} = \dot{m}(h_3 - h_4) = \dot{m}(h_1 - h_0) \qquad (3)$$

The limit heat exchange on the two sides of the IHX is:

$$\dot{Q}_{\max\_34} = \dot{m}\left(h_3 - h_{4(T_4=T_0)}\right) \qquad (4)$$

$$\dot{Q}_{\max\_01} = \dot{m}\left(h_{1(T_1=T_3)} - h_0\right) \qquad (5)$$

The objective function for the optimization is the system COP:

$$COP = \frac{h_0 - h_5}{h_2 - h_1} \qquad (6)$$

2. Results and discussion

A typical performance map is shown in Fig. 2. COP is shown as a function of the gas cooler (or condenser) pressure and of the quality at the evaporator exit. A 95/5% CO_2/DME mixture is considered (critical point at $T = 40.97°C$ and $P = 80.30$ bar). The dashed black line is the locus of the optimal vapour quality as a function of the pressure, i.e. along this line the vapour quality at the evaporator exit gives a maximum COP because the glide is 5°C. The highest COP is found at 84.54 bars, i.e. for a trans-critical cycle.

Fig. 2 shows also a continuous black line that marks a limit for the quality. On the left side of this line, the heat provided to the fluid exiting from the evaporator in the IHX is insufficient to guarantee the minimum superheat imposed at the compressor inlet, i.e. 2°C. In the case of Fig. 2, all optimal points are admissible.

Fig. 3 shows a comparison between 3 cycles using the same mixture and the same quality at the evaporator exit (point 0). The maximum COP, as shown in Fig. 2, belongs to the cycle in the middle, with a gas cooler pressure of around 90 bar. If the gas cooler pressure is raised to 110 bar, the cooling capacity is practically unchanged, while the compressor work is raised. Point 1 is shifted to the left, due to the
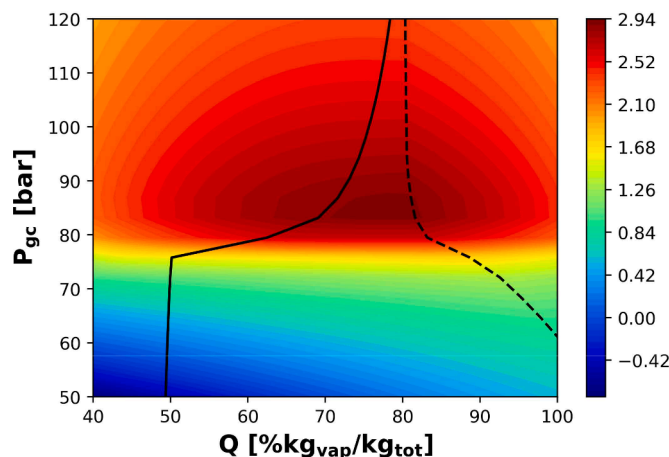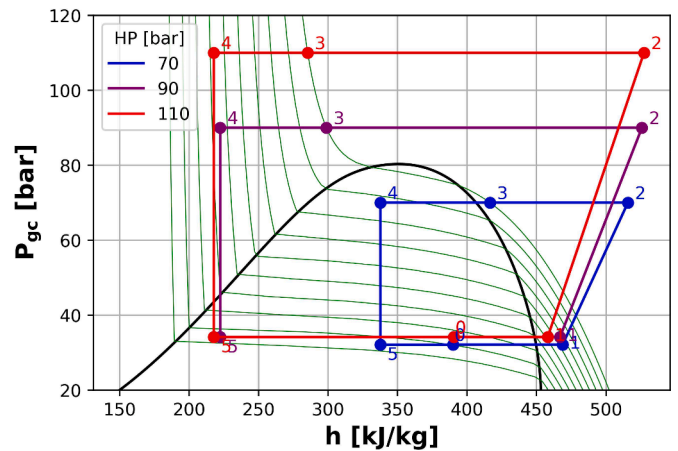

Fig. 3. Comparison of cycles with different maximum pressure for a 95/5% (in mass) CO_2/DME mixture.

reduction of the heat available at the IHX (the length of segment 3–4), due to the shape of the isotherms. The lower cycle is clearly meaningless, as the constraint on the point 3 temperature (40°C) produces a heat release to the ambient completely outside of the two-phase zone, even if the cycle is sub-critical. The IHX sees a partial condensation of the fluid, but point 5 turns out to have a high enthalpy anyway, giving a very low cooling power.

If the percentage of DME is raised to 10% in mass, the situation changes as shown in Fig. 4. The critical point is raised at $T = 49.48°C$ and $P = 84.161$ bar, hence the maximum COP is reached with a subcritical cycle. Now the dashed line is on the left of the continuous line for any pressure above 73.62 bars, i.e. all points above this pressure that give maximum COP are no longer admissible in terms of superheating at the compressor inlet.

This result may be explained by noting that the increased percentage of DME gives a higher glide and vice-versa, as shown in the diagram in Fig. 5. This diagram has been built by keeping fixed the maximum cycle pressure and the vapour quality at evaporator exit. The light-brown curve, corresponding to $x = 95\%$, shows exactly a glide of 5°C, matching the temperature drop of the cooled fluid and hence giving the maximum performance. If the DME percentage is increased to 97% (blue curve), the glide increases to 7°C. The opposite happens for lower DME percentage (e.g. green curve).

For the sake of comparison, we may show the contour map obtained with pure CO_2, which is shown in Fig. 6. In this case, the maximum COP is outside the map, due to the isothermal evaporation that cannot match
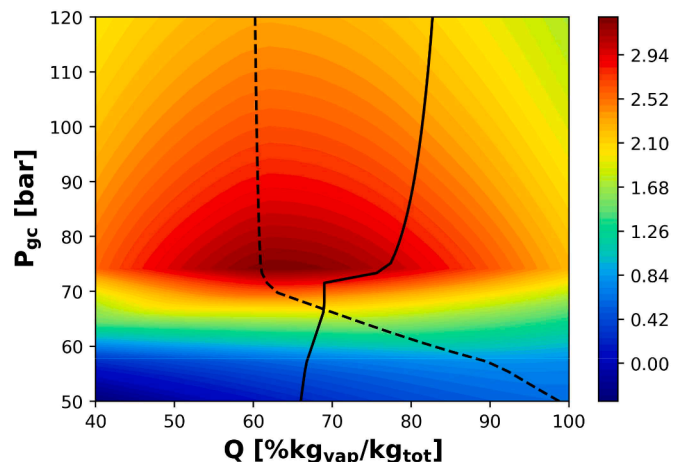

Fig. 2. Contour map of COP for a 95/5% (in mass) CO_2/DME mixture.

Fig. 4. Contour map of COP for a 90/10% (in mass) CO_2/DME mixture.
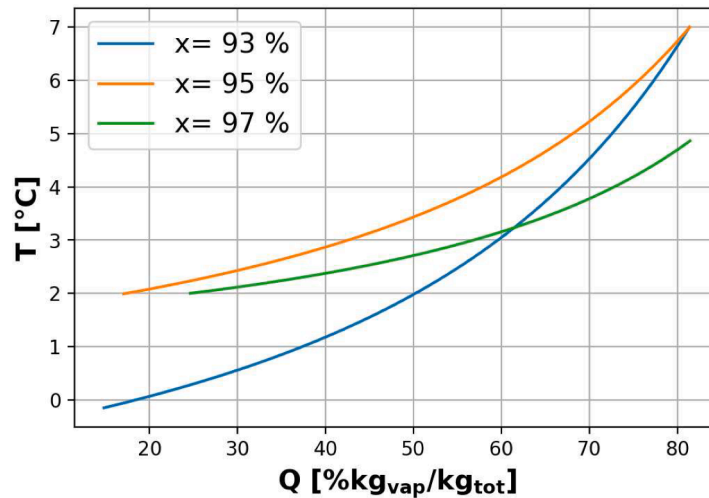
Fig. 5. Diagram of evaporator temperature for different CO_2 mass fractions at constant vapour quality at evaporator exit.
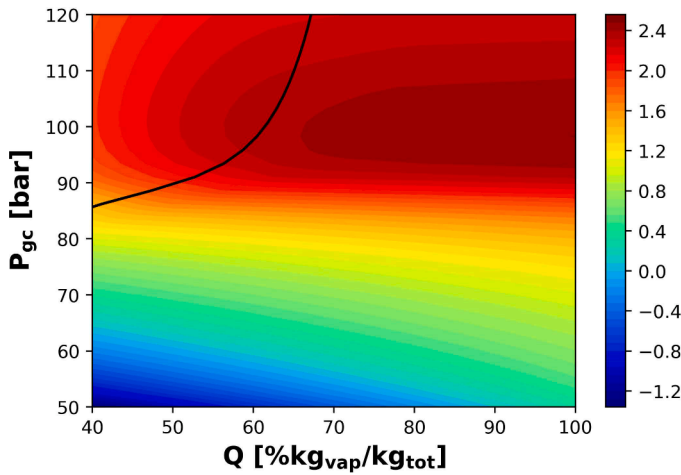

Fig. 6. Contour map of COP for pure CO_2.

the cooled fluid temperature drop even for a 100% vapour quality at evaporator exit. A better result could be obtained for a 5°C superheating within the evaporator. However, the maximum COP is significantly lower than the values found for the mixture.

All these behaviours have been summarized by collecting the optimal
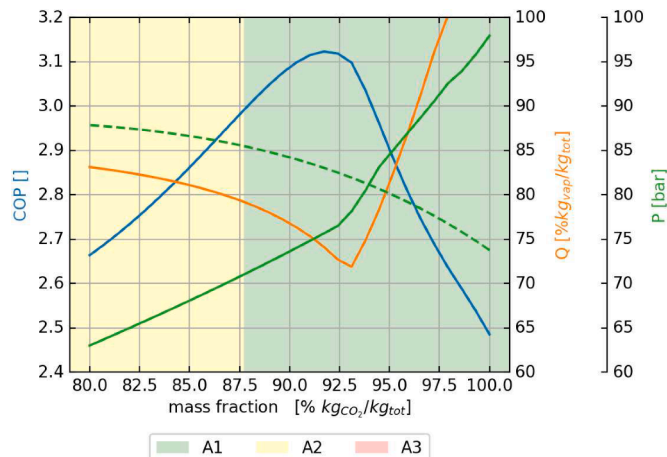

Fig. 7. Summary of results for CO_2/DME mixture.

results in the graph shown in Fig. 7. A further aspect is added, i.e. the flammability of the mixture, which has been evaluated according to Kondo et al. (2006). This paper presents a modified Le Chatelier formula, specifically applicable to mixtures of flammable and inert gases, allowing the calculation of the FIP (Fuel Inertization Point) for blends of CO_2 and several flammable substances.

The x-axis in Fig. 7 shows the mixture composition, with pure CO_2 on the right and a 80/20% mixture on the left. The mixture is non-flammable on the green zone, i.e. for a DME mass fraction below 11.8%. For higher mass fractions of DME, the mixture is mildly flammable, i.e. classified A2 according to ASHRAE Standard 34/2019.

The continuous blue line shows the maximum COP reached for a given composition by optimizing the maximum cycle pressure and the vapour quality at the evaporator exit. The highest point corresponds to a DME mass fraction of 8.08%, well within the green zone. In other words, a COP value of 3.12 may be reached with a non-flammable mixture of CO_2 and DME, while the corresponding value for pure CO_2 is 2.49. This remarkable result may be explained by considering that the mixture has an optimal pressure (continuous green line) of 75.89 bar, while pure CO_2 requires a gas cooler pressure of 97.93 bars to reach the optimum condition.

The continuous orange line shows the optimum vapour quality at the evaporator exit. The optimum COP corresponds to the minimum vapour quality. On the right of this minimum value, an increase of the mass fraction of DME produces an increased glide and hence point 0 of the cycle moves to the left on the Ph diagram in order to keep the 5°C value of glide. On the left of the minimum of the orange line in Fig. 6, the vapour quality at the evaporator exit must be increased, in order to satisfy the limit on the superheating at the compressor inlet. Hence, the glide exhibited by the mixture exceeds the 5°C value that matches the assigned temperature drop of the cooled fluid. Therefore, the COP is reduced, even if the optimum cycle pressure (and hence the compressor work) continues to decrease.

The green dashed line shows how the critical pressure decreases for decreasing the mass fraction of DME, approaching the critical pressure of pure CO_2 (73.77 bar). The intersection of this dashed line with the continuous green line shows that all optimized cycles using a CO_2/DME mixture with a mass fraction of DME higher than 6.1% are subcritical.

The cycle corresponding to the optimum condition (CO_2 mass fraction 91.9%) is shown in Fig. 8. Note that in this cycle the condenser exit (point 3) is exactly on the saturated liquid line, while the compressor inlet (point 1) is exactly at the imposed value of superheating.
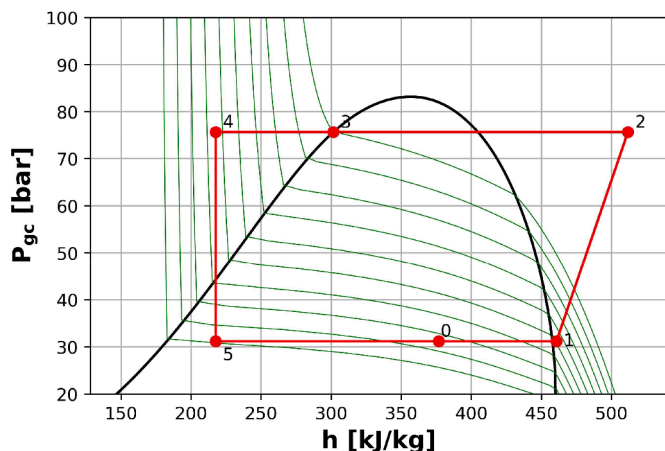
Fig. 8. Optimized cycle for CO_2/DME mixture.

2.1. Comparison of different fluids

As stated above, our objective is to explore the feasibility of a refrigeration system using a mixture of carbon dioxide and an organic compound that should improve the system efficiency, without impairing the well-known advantages of CO_2 (low GWP, high volumetric cooling capacity, absence of flammability and toxicity).

DME has been extensively dealt with in the previous part of the paper. Other fluids will be examined in this section. The first one is propane, which has been proposed by many authors as a possible candidate. The results of the calculations done with this fluid are shown in Fig. 9a.

The first point that emerges from the comparison between Figs. 9a and 7 is the maximum COP, that is 2.83 for propane against 3.12 for DME. Moreover, the optimum composition is found for a mass fraction of propane of 27.7%, which makes the mixture highly flammable (A3 ASHRAE classification).

Almost all the mass fraction range shown in the figure yields transcritical cycles, as shown by the intersection between the green dashed line (critical pressure) and the green line (optimum gas cooler pressure). The minimum vapour quality at the evaporator exit (i.e. the condition that gives a glide of 5°C) lies on the right of the maximum COP because the effect of compressor work reduction overcomes the effect of temperature matching at the evaporator.

The results gathered with CO_2/isobutane mixtures are similar (Fig. 9b), though the maximum COP is slightly higher and takes place for a lower mass fraction of the added component. The optimum composition yields a subcritical cycle. However, the optimum composition is highly flammable.

Finally, we consider CO_2/propylene mixtures (Fig. 9c), which give the highest COP among all the substances considered herein. The maximum cycle pressure is lower than 70 bar in the optimum zone. However, this good result is obtained for a mass fraction of propylene above 20%, well within the range of high flammability.

We may conclude that propane, isobutane and propylene may give a benefit in terms of performance when added to CO_2, but this result is gathered only when the added substance has a mass fraction that makes the mixture highly flammable. From a practical point of view, this makes these mixtures scarcely attractive with respect to the pure hydrocarbons, which give even higher performance.

2.2. Effects of the ambient temperature

Up to now, a fixed temperature has been set at the gas-cooler or condenser exit, i.e. the ambient condition has been left unchanged. If the ambient temperature is lowered and hence the condenser may work at a lower temperature, the results change as shown on top of Fig. 10, where
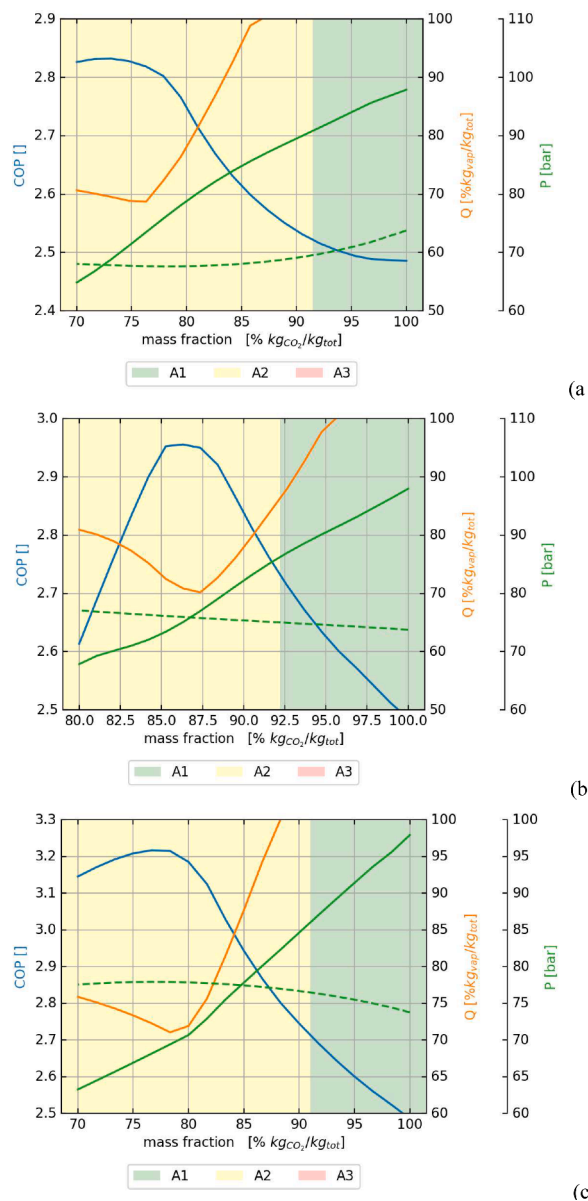

(a

(b

(c

Fig. 9. Summary of results for mixtures of CO_2 and propane (a), isobutane (b), propylene (c).

a condenser exit temperature of 30°C has been chosen.

According to the findings reported in the previous section, only mixtures of CO_2 and DME are used. For an easy comparison, the results for condenser exit temperature of 40°C already shown in Fig. 7 are copied in the middle part of Fig. 10 on the same range of mass fractions. The first evident feature is the downward movement of the COP curve (the blue one) going from the top graph to the bottom one.

Moreover, the optimum mass fraction of DME moves to the left, i.e. more added fluid is required if the condenser exit temperature (i.e. the ambient temperature) is raised. This may be understood considering that, if point 3 of the cycle (exit of the condenser or gas cooler) moves upward and to the right, even considering the slight variations in the IHX operation, the whole expansion 4–5 moves rightward. Therefore, the evaporation 5–0 is shortened and a higher fraction of DME is required to give the assumed 5°C glide.

The top graph in Fig. 10 shows that all the COP curve (blue line) is higher with respect to the one shown in the middle graph. This means that, for any mass fraction of DME, the reduced temperature at point 3 is highly beneficial. For example, if the system has been optimized for T_3
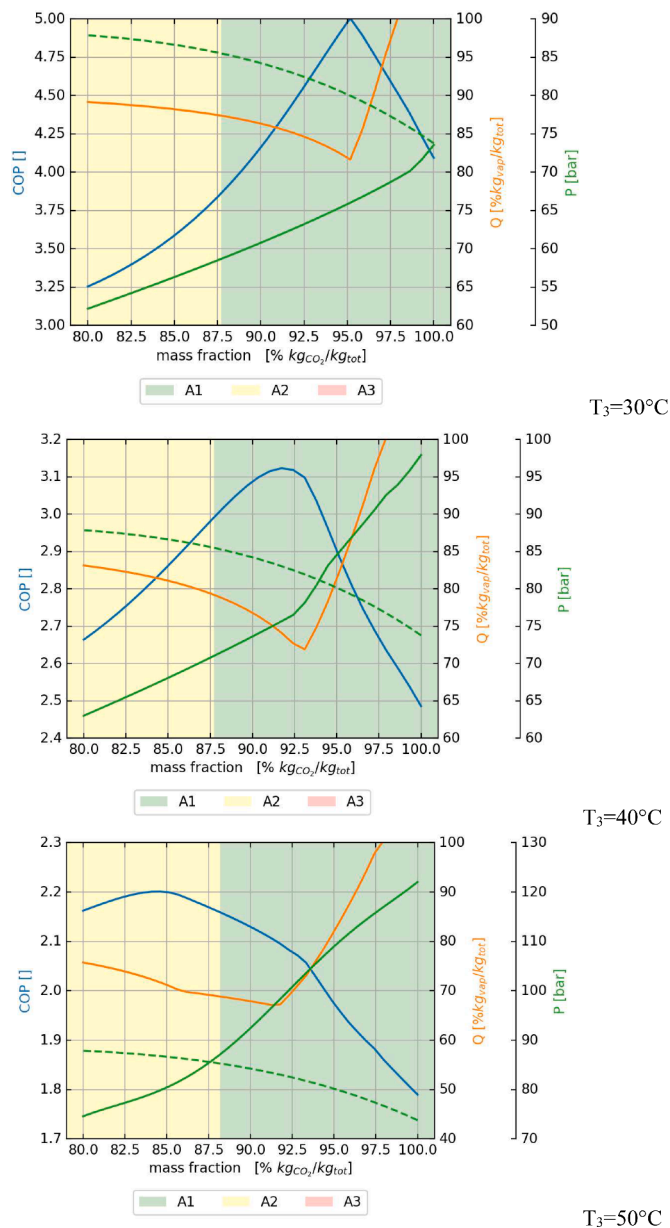
Fig. 10. Summary of results for CO_2/DME mixture as a function of condenser exit temperature.

$= 40°C$ as in the middle graph in Fig. 10, the optimum CO_2 mass fraction is 91.92%, as already stated. If a system featuring this fluid composition is operated at $T_3 = 30°C$, the upper graph gives a COP of 4.46, which is not the absolute maximum (≈ 5) that would be reached with a mixture specifically optimized for $T_3 = 30 °C$ (i.e. CO_2 mass fraction = 95.15%), but is anyway significantly higher than any COP attainable with $T_3 = 40°C$.

On the opposite, as shown in the lowest graph in Fig 10, if the condenser exit temperature is raised to 50°C, the COP lowers, showing a maximum of 2.2 for a mixture composition with about 85% of CO_2. This optimum is located in the yellow part of the diagram, which means that the mixture is flammable (A2 classification). The optimum gas cooler pressure is now around 80 bar, i.e. around 4 bar higher than that shown in the middle graph. Note that, while in the two uppermost diagrams the maximum COP is in the zone of the lowest vapour quality at evaporator exit (yellow curve), in the lowest graph the two points are located at different compositions.

As explained in the comment to Fig. 7, the minimum quality at

evaporator exit represents the optimum operation of the evaporator in terms of glide. In the case of the bottom graph in Fig. 10, this optimum corresponds to a very high condenser pressure, i.e. a very high compressor work. Apparently, this counterbalances the effect of the evaporator optimization and shifts the optimum mixture composition to the left. If the mixture is optimized for operating with $T_3 = 40°C$ (i.e. CO_2 mass fraction 91.92%), the COP at $T_3 = 50°C$ is further lowered to 2.1. Even so, this composition is preferable, as it gives a non-flammable working fluid. A potential drawback of this choice is that it gives a supercritical operation for high ambient temperature.

3. Conclusions

The thermodynamic analysis presented above shows that mixtures of CO_2 and organic compounds, such as propane, isobutane, DME and propylene, may increase the COP of refrigeration cycles thanks to a reduction of compression work and an improved temperature matching between the evaporating working fluid and a finite-heat-capacity heat source. The best results are obtained with a mixture of CO_2 with a 23% mass fraction of propylene, which guarantees a COP increase of 28%. However, this mixture, as well as those containing propane and isobutane, is highly flammable. Therefore, they may hardly compete with pure hydrocarbons, which give even higher performance.

On the other hand, adding CO_2 with 8% of DME gives a COP increase of 25%, but the mixture is non-flammable. Therefore, this mixture would represent a safe option, combining the advantages of CO_2 (low GWP, high volumetric cooling capacity) with good energy efficiency, even for a basic cycle comprising only an internal heat exchanger. By the way, DME has GWP=1, so that the direct emission term in the TEWI calculation for the CO_2/DME mixture is negligible. The 25% reduction in energy consumption with respect to pure CO_2 translates in an equal reduction of indirect emission (i.e. on the whole TEWI, direct emission being negligible). In other words, the proposed mixture would allow a low TEWI without requiring complicated plant layouts, even if, obviously, improved configurations may be explored. This result may be a first suggestion towards future experimental activity.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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