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REFRIGERATION CYCLE PERFORMANCE USING CO₂ (R744) BLENDS TO OTHER NATURAL REFRIGERANTS

Matheus Henrique Cavaleiro Garros¹

Robson Leal da Silva^{1,2}

¹UFGD – Universidade Federal da Grande Dourados, FAEN – Faculdade de Engenharia, Dourados-MS, Brasil, CEP: 79.804-970

²PEM – Programa de Pós-Graduação em Engenharia Mecânica, UEM – Universidade Estadual de Maringá, Maringá-PR, Brasil, CEP: 87.020-900

matheus.garros@gmail.com

robsonsilva@ufgd.edu.br

Abstract. Natural refrigerants are the best solution to reduce global warming, due to their low GWP. R744 has already been used in many applications, but for transcritical cycles, the performance is lower than the observed on other natural refrigerants cycles. This paper investigates the performance of R744 blends to other natural refrigerants, to evaluate performance enhancements. The research was carried out using the open-source software DWSIM, and the fluids used in the blends were R717, R600a, and R290. The reference synthetic fluid to analyze the results was R134a. The main findings are that all the blends are able to increase the COP, and with R717 it is possible to achieve almost the same levels as R134a. Also, a decrease on 2nd law efficiency is noticed, and it is worse for the hydrocarbons, mainly R600a, which had efficiencies near zero for evaporation temperatures close to 0°C. Mass flow rate and operational pressures are reduced, a great achievement, since the R744 cycle has high operational pressures. The present research shows improvements in R744 transcritical cycles, regarding COP, refrigerant charge, and operational pressures.

Keywords: transcritical, GWP, COP, exergy.

1. INTRODUCTION

The Montreal and Kyoto Protocols are two global agreements to reduce the emissions of gases which collaborate to ozone layer destruction and global warming. The Kigali amendment (Montreal Protocol) has already set a deadline for the utilization of HFCs due to their high levels of GWP (Global Warming Potential). The refrigerant alternatives with low GWP are the well-known natural refrigerants, so the big challenge for the next years is to establish the natural refrigerant technology in air conditioning and commercial refrigeration applications (GTZ, 2008).

Several studies have been carried out to evaluate R744 mainly. In cold climates, it is a good option due to the operation in a subcritical cycle, but many systems are operating in transcritical cycles, as well as studies regarding it (Bellos and Tzivanidis, 2019; Flores et al., 2020).

Neto et al. (2019) point some of the R744 notable properties: It is not harmful to the ozone layer, it has very low GWP, it is non-toxic, non-flammable, and non-corrosive, and since it is abundant in the environment the costs of the fluid are very low, and it can be discarded to the atmosphere. Some other characteristics discussed are the high levels of volumetric efficiency, and low-pressure drop while in heat exchangers or tubulations, and the remark to transcritical cycles: It operates in high pressures, and since there is no condensation of the fluid in the gas cooler, every change in the temperature will lead to another optimum compressor outlet pressure. It means that for each operational condition, there is an optimum compressor outlet pressure that maximizes the COP.

In hot climates, with temperatures that are around 30°C, it would be almost impossible to have R744 subcritical cycles, due to its low critical temperature (around 31°C), without using a cascade cycle, allowing R744 to condense during the heat rejection process. In transcritical cycles, the output temperature of the heat rejection process will be higher than the critical temperature, meaning that there will be no liquid on the high-pressure side of the line for the classical vapor compression cycle, because of that, those cycles are said to have a gas cooler instead of a condenser.

1.1 Objectives

There are some typical refrigeration cycles: a) Vapor-Compression – VC; b) Absorption Refrigeration – AR; c) Evaporative Cooling – EC, that can reduce air temperature by 15°C and are best suited for dry climates; d) Thermoelectric Cooling – TEC (Yu et al., 2020) that uses electric current and a thermocouple, causing a cooling effect by the Peltier Effect.

As typical transcritical VC cycles for R744 as working fluid are not as good as conventional phase-change VC cycles, an interesting option is to evaluate if those cycles can have COP improvements when using R744 and low GWP refrigeration fluids blends. Therefore, the main objective is to investigate R744 blends to other natural refrigerants and identify combinations that provide performance improvement. Criteria for best performance considers energy and exergy efficiency (1st and 2nd Laws of Thermodynamics), mass flow rate, operational pressure and compressor outlet temperature.

2. METHODOLOGY

2.1 Thermodynamic Cycle (VC) and Working Fluids

The diagram on Figure 1 represents a basic 4 state VC refrigeration cycle (compressor, condenser/gas cooler, throttling valve and evaporator), it shows a comparison between two R744 cycles operating on the exact same conditions, except the post gas cooler/condenser temperature. In image (a) the cycle operates on a 15°C condition, and on (b) in a 35°C condition. The two main differences between a subcritical and a transcritical R744 cycles can be observed: higher operational pressures for the same evaporation temperature, and higher mass flow rate (due to the lower enthalpy difference on the evaporator – bottom region of the colored lines) to achieve the same refrigeration capacity.

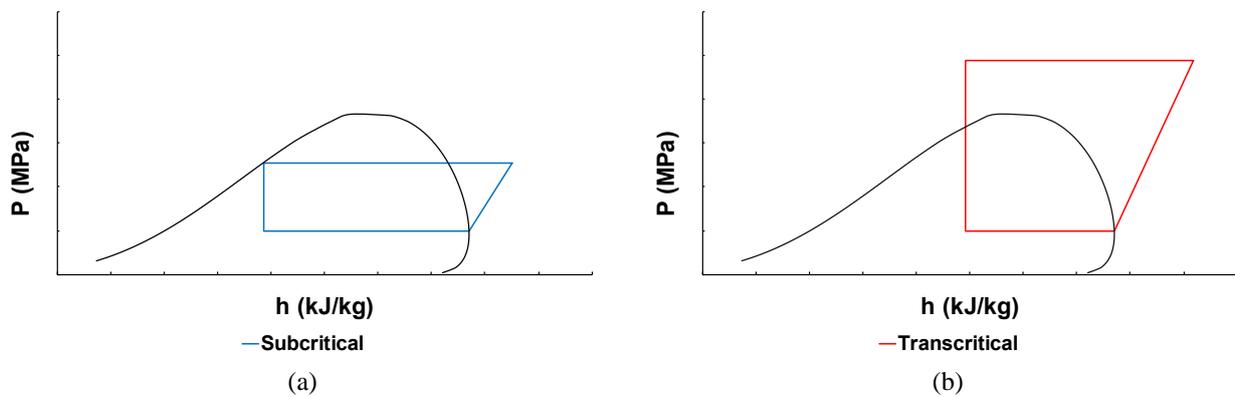


Figure 1. Subcritical (a) and transcritical (b) R744 refrigeration cycles

Figure 2 shows the models used in the development of this work. The cycle configuration analyzed was the classic 4 stage refrigeration cycle combined with an internal heat exchanger, as shown in (a). The criteria for Thermodynamics 2nd Law or exergy efficiency, is applied considering the diagram in (b), considering the three exergy transportation forms: mass flow rate, work (mechanical power), and heat (thermal power), by convention they're positive on the direction displayed below.

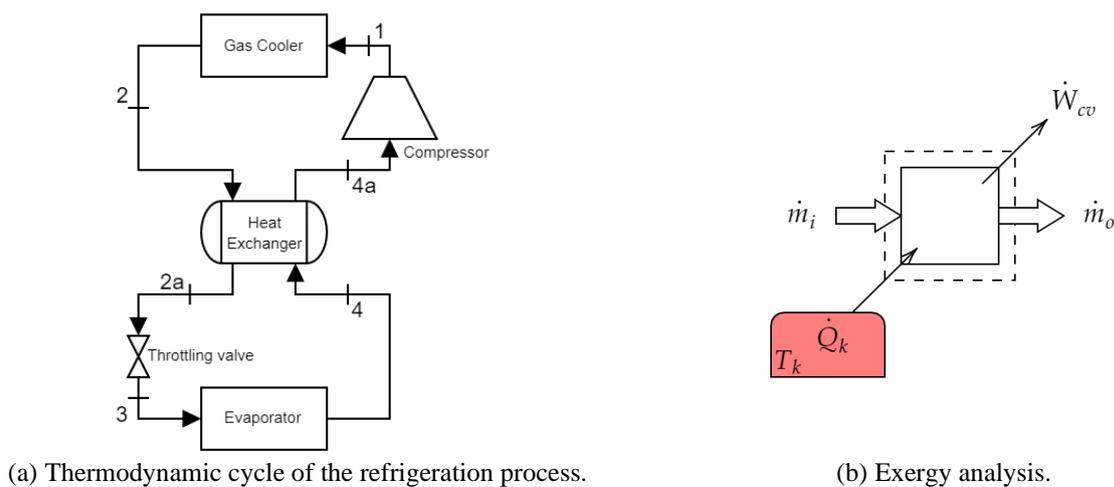


Figure 2. Proposed models

A comparison between the chosen working fluids is shown in Table 1.

Table 1. Refrigerant characteristics

Refrigerant	Flammability	Toxicity	GWP ⁽¹⁾
R134a	None	Low	1300
Carbon dioxide (R744)	None	Low	1
Ammonia (R717)	Low	High	0
Isobutane (R600a)	High	Low	3
Propane (R290)	High	Low	3

⁽¹⁾Goetzler et al. (2014)

2.2 Mathematical Formulation

All equations considered for energy and exergy analysis are presented next. The mechanical and thermal power by the compressor (required) and gas cooler (rejected), respectively are Eq. (1) and (2). Following, the thermal power absorbed by the evaporator (refrigeration capacity) and the coefficient of performance (1st Law of Thermodynamics) are in Eq. (3) and (4). The COP is the energy efficiency, 1st law of Thermodynamics criteria to identify best working fluid blends.

$$\dot{W}_c = \dot{m}(h_1 - h_{4a}) \quad (1)$$

$$\dot{Q}_{gc} = \dot{m}(h_1 - h_2) \quad (2)$$

$$\dot{Q}_e = \dot{m}(h_4 - h_3) \quad (3)$$

$$COP = \frac{\dot{Q}_e}{\dot{W}_c} = \frac{h_4 - h_3}{h_1 - h_{4a}} \quad (4)$$

The general form to exergy destruction in steady state regime (Çengel and Boles, 2011) for the refrigeration system is expressed by Eq. (5), and Eq. (6) represents the specific exergy contribution from enthalpy and entropy at a reference state ("0"), set as 25°C and 101.325 kPa (1 atm at sea level).

$$0 = \sum_k \left(1 - \frac{T_0}{T_k}\right) \dot{Q}_k - \dot{W}_{cv} + \sum_i \dot{m}_i e_i - \sum_o \dot{m}_o e_o - \dot{E}_d \quad (5)$$

$$e = h - h_0 - T_0(s - s_0) \quad (6)$$

Applying Eq. (5) for each system's component (or process), it is possible to obtain each exergy destruction contribution. For the compressor, considering it as adiabatic and with mechanical power input we have Eq. (7), while for the gas cooler and its thermal power input results in Eq. (8).

$$\dot{E}_{d,c} = \dot{m}T_0(s_1 - s_{4a}) \quad (7)$$

$$\dot{E}_{d,gc} = \dot{m}T_0 \left[\frac{(h_1 - h_2)}{T_2} - (s_1 - s_2) \right] \quad (8)$$

For the heat exchanger, with 2 inlets and 2 outlets, without heat or work going in or out the boundaries of the equipment, is represented by Eq. (9). As for the throttling valve, bearing in that, by definition, there is none kind of thermal or mechanical power, there is only mass flow rate contribution to exergy destruction, Eq. (10). And for the evaporator, with thermal power input, Eq. (11).

$$\dot{E}_{d,hx} = \dot{m}\{[(h_2 + h_4) - (h_{2a} + h_{4a})] - T_0[(s_2 + s_4) - (s_{2a} + s_{4a})]\} \quad (9)$$

$$\dot{E}_{d,tv} = \dot{m}T_0(s_3 - s_{2a}) \quad (10)$$

$$\dot{E}_{d,e} = \dot{m}T_0 \left[\frac{(h_3 - h_4)}{T_4} - (s_3 - s_4) \right] \quad (11)$$

Then, the total exergy destruction in the refrigeration system is the sum of contributions from each component (or process), given by Eq. (12).

$$\dot{E}_{d,t} = \dot{E}_{d,c} + \dot{E}_{d,gc} + \dot{E}_{d,hx} + \dot{E}_{d,tv} + \dot{E}_{d,e} \quad (12)$$

The second law efficiency is given by Eq.(13), and an alternative expression (for refrigeration cycles) is also provided in Eq. (14), both from Çengel and Boles (2011).

$$\eta_{II} = 1 - \frac{\text{Exergy destroyed}}{\text{Exergy provided}} = 1 - \frac{\dot{E}_{d,c} + \dot{E}_{d,gc} + \dot{E}_{d,hx} + \dot{E}_{d,tv} + \dot{E}_{d,e}}{\dot{W}_c} \quad (13)$$

$$\eta_{II}^* = \frac{COP}{COP_{rev}} = COP \left(\frac{T_2 - T_4}{T_4} \right) \quad (14)$$

For refrigeration cycles using blends of working fluids, it is required to define the temperature glide, for further analysis, Eq (15).

$$Tg = T_4 - T_3 \quad (15)$$

2.3 Simulation Procedures

The proposed cycle (Figure 2) is investigated for several operational conditions. First, the evaporator inlet temperature (T3) is evaluated from -30°C up to 0°C, with a 10°C step. The gas cooler outlet temperature (T2) was fixed on 35°C. For each one of T3 values, there are 4 (four) refrigeration fluids to consider, first as pure composition (R134a, R744, R717, R600a, and R290) and next the R744 blends. To investigate the performance of the different blends, each one of the three natural fluids (R717, R600a and R290) were gradually incorporated to R744 cycle, with a 25% step (75%, 50%, and 25% of R744 in mass). The reference systems for performance comparison are R134a and R744, both for pure substances (100%).

The present research was carried out through computational simulations using the open-source software DWSIM (Mariani et al., 2019; Mastellone et al., 2020). The Peng-Robinson property package was used in order to estimate the mixtures properties. Each condition has its simulation results optimized using the Brent Constrained method (Brent, 1973) present in DWSIM. It finds the optimum compressor outlet pressure which maximizes the COP. The cycle reference parameters, i.e., boundary conditions, are summarized in the Table 2.

Table 2. Cycle conditions

State	Condition
1	Optimized pressure for COP maximization
2	35°C, for all simulations
3	-30°C to 0°C, with a 10°C step
4	X = 1, saturated vapor

Other assumptions regarding the simplifications of the thermodynamic cycle:

- Steady state operation;
- No pressure drop in the gas cooler, evaporator or heat exchanger;
- Isentropic efficiency of the compressor: 85%;
- Heat transfer efficiency on the internal heat exchanger: 75%. This value is used to find the actual heat transfer, multiplying it by the estimate of the maximum heat transfer, calculated by checking the inlet streams properties (Wagner, 2021). In the case of the heat transfer effectiveness, a temperature difference ratio would be the calculation method;
- Ideal throttling valve, inlet enthalpy is equal to outlet enthalpy;
- In order to determine the mass flow rate, the refrigeration capacity was set as 1 kW to all simulations.

3. MODEL VALIDATION

The proposed cycle was compared with the simulations executed by Bellos and Tzivanidis (2019), performed using EES (F-Chart Software, 2004). Cycle and model validation results obtained are in Table 3, displaying the relative error to the reference values for: COP, outlet compressor pressure, and mass flow rate. using the same cycle and boundary

conditions as them, to a 35°C gas cooler outlet temperature and several evaporation temperatures (T_e), using R744 as the refrigerant.

Table 3. Validation results

T_e (°C)	Δ COP	ΔP_c	$\Delta \dot{m}$
-35	-11.25%	13.01%	-1.55%
-25	-8.94%	8.91%	1.01%
-15	-8.43%	6.23%	3.12%
-5	-8.57%	4.37%	5.09%
5	-9.23%	2.97%	7.29%

The relative errors were always close to 10% and can be justified by the use of the thermodynamic model (Peng-Robinson), which has an uncertainty value associated. Since fluid blend properties are not available like pure substances properties (in libraries and tables), those values differences seem to be acceptable.

4. RESULTS AND DISCUSSION

Figure 3 shows the performance values for COP. For all the simulations the COP increased with the increase of T_3 . Since higher temperatures are demanded on state 3, a lower expansion is needed. It heads to higher pressures on the inlet of the compressor, which decreases the pressure ratio and, as a consequence, the power required, increasing the COP, due to the constant refrigeration capacity. For the pure fluids, the COP was about ~3-6 including R-134a, exception for R744 that has lower COP values ~1-3.

It is notable COP rises when one of the three fluids are blended to R744. For the ammonia system, the COP almost didn't change with the increase of R717 showing good results, since the COP of the R717 cycle was near the objective R134a. For the hydrocarbons a different behavior can be observed, the COP for the 75% of R744 cycles have a higher value for R600a than R290. For 50% both showed almost the same values, and for 25% R290 was slightly better.

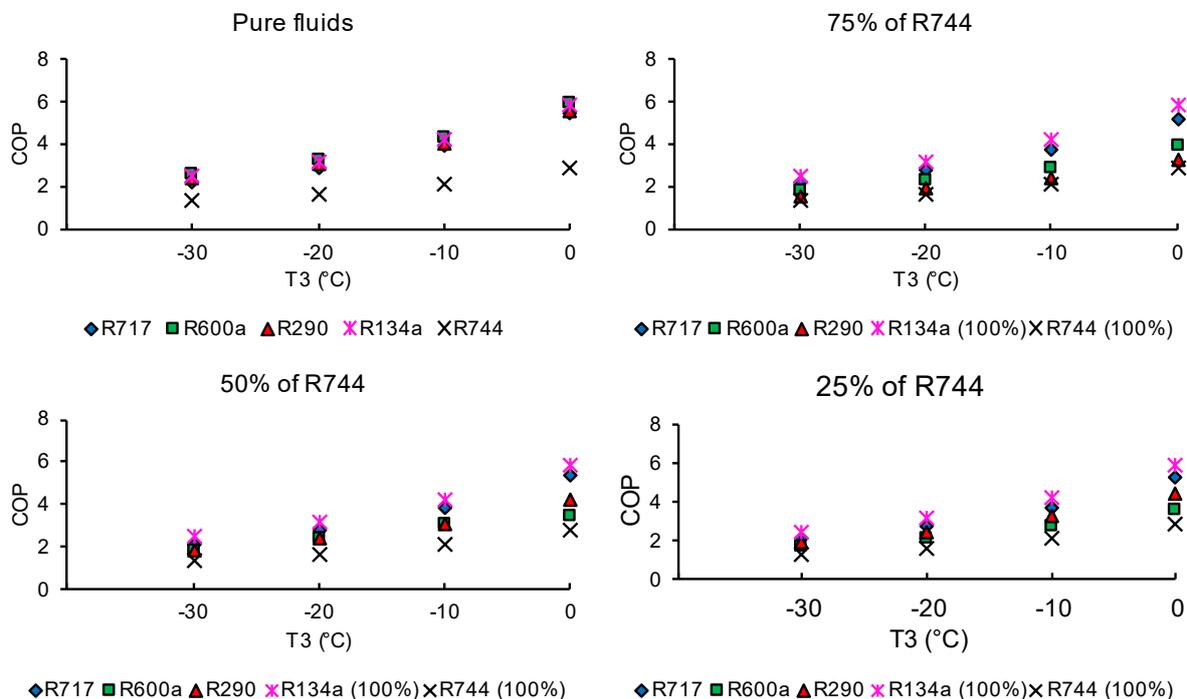


Figure 3. COP for each set of simulations.

Figure 4 shows the 2nd law efficiency, which slightly increases with T_3 for the pure fluids (R134a and natural ones), whereas, tends to decrease with the increase of T_3 for all the blends – values stood near the original R744 value or worse. This indicates even though a COP increase happens, the simulated cycle gets far from the ideal reversible cycle. The best results are for R717, being near the original R744 cycle. A negative second law efficiency was achieved in the R600a cycle with the 50/50 blends because the total exergy destroyed is bigger than the exergy provided to the system. This negative value occurs due to T_4 higher than T_2 , Eq. (14), an aspect that will be discussed further below. Finally, while

the performance of R290 blends is better than R600a blends, it is not as good as R717 blends, and neither is better than the objective R134a cycle.

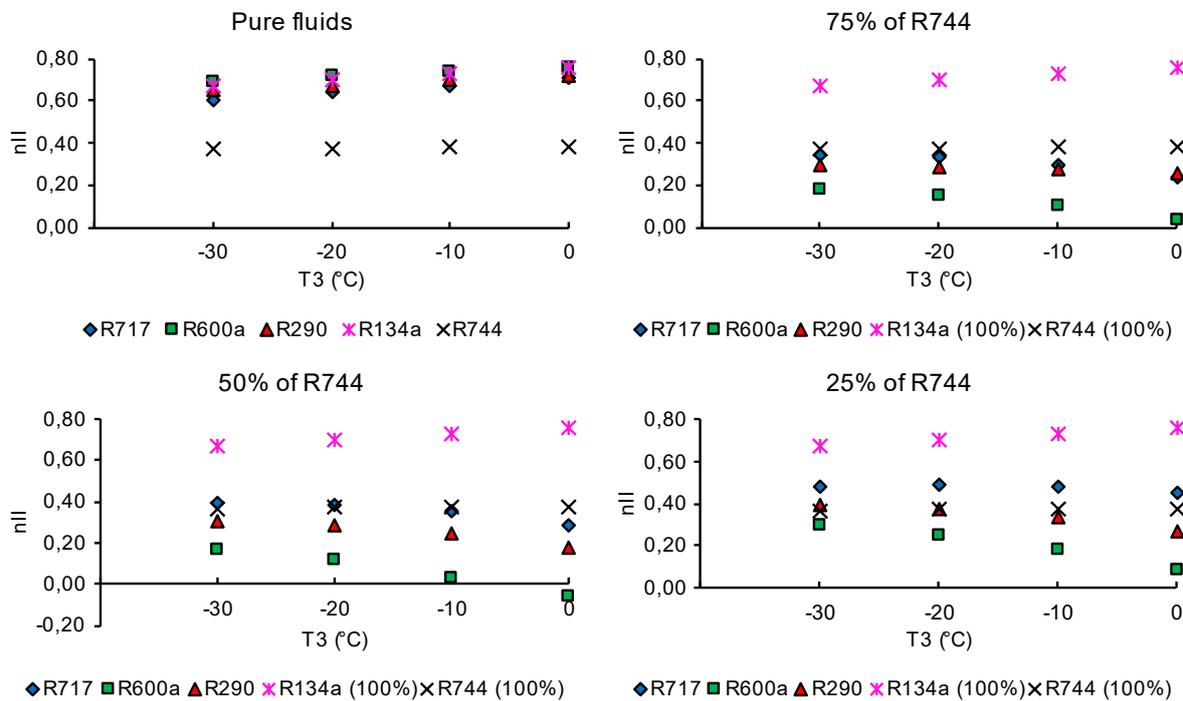


Figure 4. 2nd Law efficiency for each set of simulations

Next, in Figure 5, the temperature glide (T_g) behavior is discussed. Pure fluids have phase changing under constant temperature and pressure, but fluid blends can change the way a phase transition happens. For zeotropic compound mixtures, the condensation and vaporization can be described by a temperature glide, which means a temperature change for a constant pressure that occurs on the evaporator. As a result, for each pressure during a phase changing, a different temperature glide happens. As an example, for R744/R290 in 75/25 mass proportion blends (Figure 5a), the bubble point corresponds to the moment where the first bubbles start to appear on the mixture, and the dew points, where the mixture starts condensing. Pure compounds would not be in a phase mixture, as observed in the points between the two curves.

The temperature glide is the most important parameter when designing a system operating with a refrigeration fluid blend since it will define T_4 , the outlet temperature of the evaporator, and the lowest temperature that can be achieved in the refrigerated space. In Figure 5b, for 50% of R744 to $T_3 = 0^\circ\text{C}$ a temperature gliding of almost 45°C is reached when using R600a. It means that the temperature required for the complete blend to evaporate is higher than T_2 . That same condition explains the simulation results in negative values for η_{II} (R600a and $T > -10^\circ\text{C}$), Figure 4.

The lowest T_g values occur for R717 and R290 cycles, both results are near each other and have small differences in the whole T_3 range. For the hydrocarbons, the 50/50 and 25/75 compositions were the ones with the highest values for T_g and the lowest is for R717 (Ammonia), while in 75/25 blend for R290 have smaller values than R-717 (Ammonia). A general behavior is that T_g has small decreases as T_3 goes from -30°C up to 0°C at 75/25 blends, almost constant T_g for 50/50 blends, and small increases for 25/75 blends. It seems to be an effect of R744 higher mass in the 75/25 blends, and that influence diminishes as hydrocarbons and ammonia mass increases for 50/50 and 75/25 blends.

So, in general, the 2nd law efficiency tends to drop because the proportion of the exergy destroyed and provided increases with T_3 , due to the temperature gliding, which means higher T_4 temperatures, increasing the COP for a reversible cycle operating between the same T_2 and T_4 temperatures.

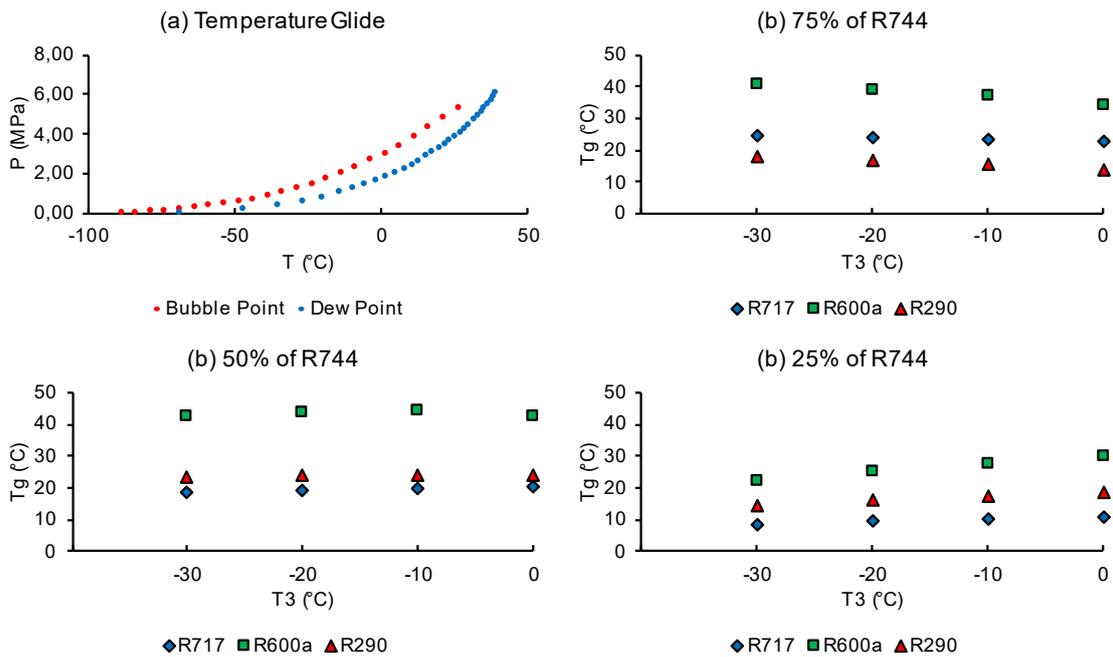


Figure 5. Peng-Robinson results for a 75/25 mass proportion of R744/R290 (a) and Temperature gliding for each set of simulations (b).

The total exergy destruction tends to decrease as T_3 increases, see Figure 6. The following contribute to lower exergy destruction: As T_3 increases, the throttling valve can perform a lower expansion, and it leads to higher pressure on 4a, and a lower compression in 4a to 1; thus, T_1 will decrease, and less heat will be rejected in 1 to 2 (gas cooler).

The best results, and closer to the R134a cycle, e.g., lower exergy destruction, are for R717 blends, in comparison to other natural refrigerants. The R744/R600a blends almost didn't change the total exergy destruction, standing close (and sometimes higher than) the original R744 cycle. For R290 the decreasing of R744 leads to better results, but not as notable as R717.

Given that R744 operates in a transcritical cycle, adding almost any commercial natural fluid (assuming that they're not critical on the gas cooler outlet) can reduce the exergy destruction. The only exception is R600a, so connecting it to the temperature glide, it is possible to say that the higher the temperature glide, the lower the reduction on the exergy destroyed.

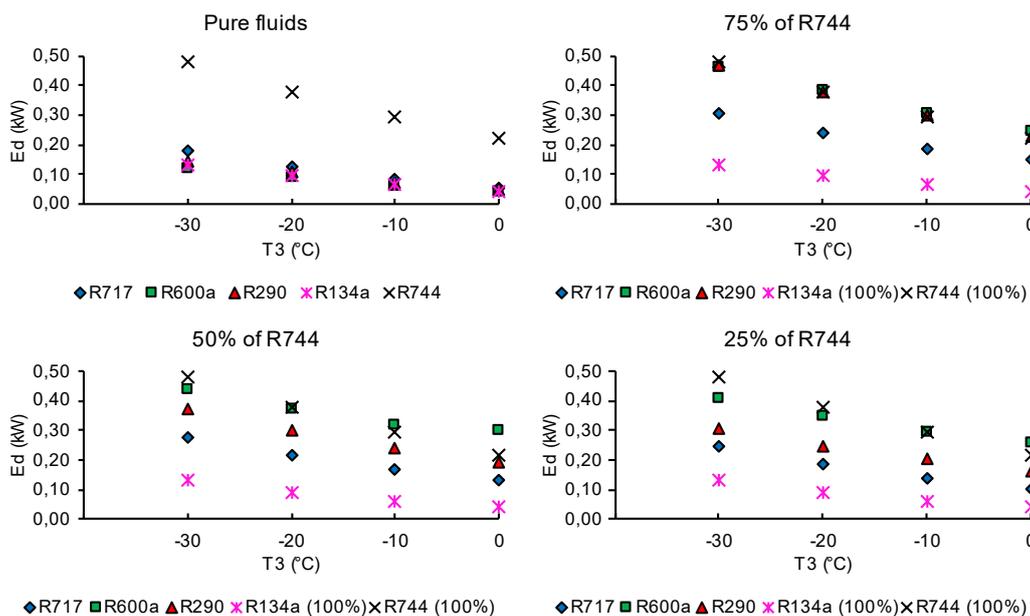


Figure 6. Total exergy destruction for each set of simulations.

Figure 7 represents the relative mean exergy destruction distribution by component, for all the four T3 temperatures. For the pure fluids, the exergy destruction happens mainly in the compressor (Edc), except for the R744 and R717, which have a high heat rejection due to high temperatures on state 1. For the blends, from 25% to 50% of R744 the greater participation is from the gas cooler (Edgc), to 75% it changes to the throttling valve (Edtv). For all the blends a higher proportion of exergy is destroyed on the evaporator, even though the total exergy destroyed reduces (Figure 6). For the pure fluids, the evaporator (Ede) has a near zero participation, and, for the blends, the heat exchanger (Edhx) has this characteristic instead.

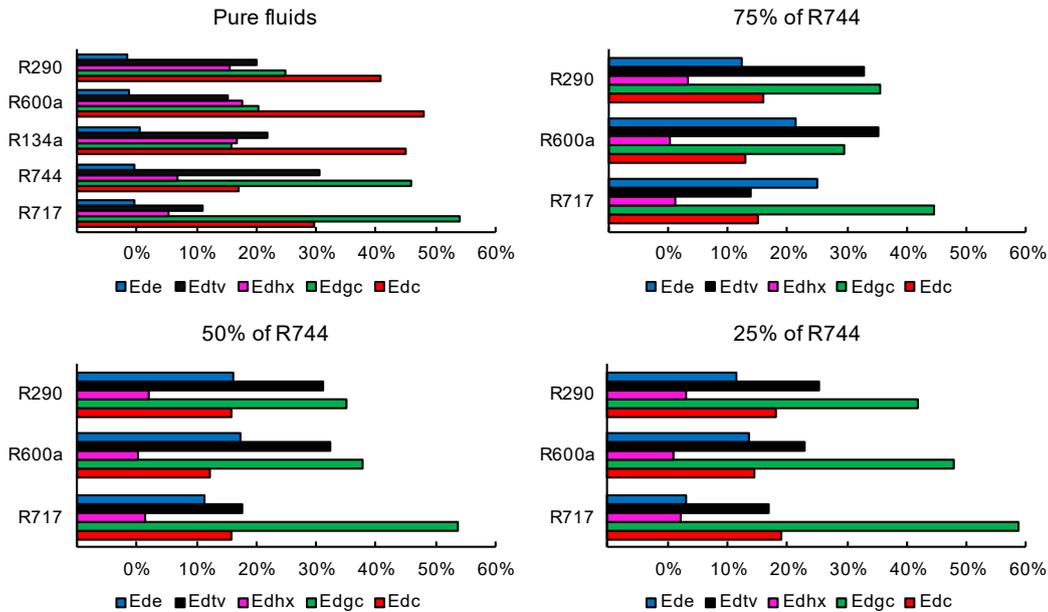


Figure 7. Mean relative exergy destruction by system component for each set of simulations.

The mass flow rate changes are shown in Figure 8. For the pure fluids, the R744 cycle and R134a have similar mass flow rates, and with the adding of other refrigerants on the R744 cycle the values obtained got better, showing a decrease in the mass flow rate necessary to attend the same refrigeration capacity. The R717 cycle showed the best results, but all the three blends are proved to being able to decrease the fluid charge, mainly for compositions of R744 lower than 75%.

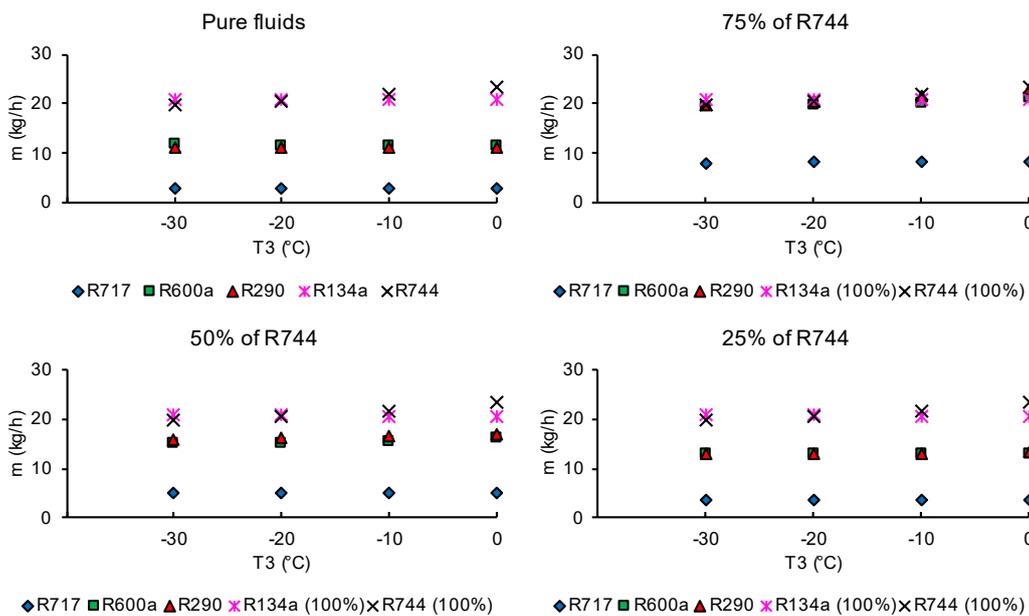


Figure 8. Mass flow rate for each set of simulations.

Table 4 summarizes the pressure and temperature data for state 1 (gas cooler inlet and compressor outlet). It is remarkable that P1 values have decreased for all R744 blends comparing to R744 (100%). Nevertheless, for the R744/R717 blends present an increase on T1 for all T3, probably due to R717 (pure), which already has higher temperatures values than R744 (pure). In general, the pressure and temperature achieve intermediate values between the original R744 cycle and the simulated data for the other natural fluids used in the blends.

Table 4. Compressor outlet pressures and temperatures

Scenarios	P1 (MPa)					T1 (°C)					
	T3 (°C)	R744	R134a	R717	R600a	R290	R744	R134a	R717	R600a	R290
Pure	-30	9.54	0.84	1.35	0.47	1.23	197.22	104.45	256.64	90.49	102.54
	-20	9.30	0.84	1.35	0.47	1.23	165.69	90.69	209.18	79.57	89.91
	-10	9.08	0.84	1.35	0.47	1.23	137.24	78.39	167.93	69.77	78.41
	0	8.87	0.84	1.35	0.47	1.23	111.15	67.32	131.83	60.91	67.83
75% R744	-30			4.81	6.08	7.17			207.76	143.66	153.91
	-20			4.81	6.08	6.99			174.49	126.46	132.89
	-10			4.81	6.08	6.85			144.91	110.33	114.08
	0			4.81	6.08	6.69			118.35	94.92	95.27
50% R744	-30			3.33	4.65	4.81			236.83	143.40	135.23
	-20			3.33	4.65	4.81			195.47	129.06	119.47
	-10			3.33	4.65	4.81			159.81	116.06	104.98
	0			3.33	5.19	4.81			128.66	108.09	91.39
25% R744	-30			2.24	2.85	3.14			259.08	141.36	128.84
	-20			2.24	2.85	3.14			211.62	127.97	114.33
	-10			2.24	2.85	3.14			170.71	116.09	101.13
	0			2.24	2.85	3.14			135.16	105.45	88.93

Suggestions for future investigations are to promote drop-in replacement in experimental refrigeration systems, using R744 transcritical cycles and blends to HC's and Ammonia. Natural refrigerants as working fluids are low GWP solution without changing the cycle structure, like adding stage-compressors, intercoolers, and cascade cycles.

5. CONCLUSIONS

All the blends for CO₂ (R744) and natural refrigerants (HC's and Ammonia) are able to increase the system performance according to 1st Thermodynamics law criterion (\uparrow COP), but at the same time it is worst for 2nd Thermodynamics Law criterion (\downarrow η_{II}). The COP values reach close values to R134a cycle, and R744/R717 blends can achieve almost the same levels.

The temperature increase on the evaporator (temperature glide) has a significant negative effect on the 2nd law efficiency of R744/R600a blends, becoming even higher than T2 (gas cooler outlet temperature). In the other cases, blends do not improve the 2nd Law efficiency, since it is not possible to surpass the original R744 cycle. Temperature glide behavior is the same for all the blends, increasing with T3 for 75% R744 blends and decreasing with T3 for 25% R744 blends, being Tg inclination curve a direct function of R744 mass proportion in the cycle.

Exergy destruction shows a notable decrease as T3 increases and decrease in R744 mass proportion, for blends with R717 or R290. Exergy destruction by component also changes for different blends, increasing the proportion of exergy destroyed on the evaporator for all the conditions.

At last, to attend to the same refrigeration capacity, the refrigeration system requires lower mass flow rate (less weight) and lower operating pressures when using natural refrigerants blends (hydrocarbons and ammonia) with R744 in comparison to the pure R744 and R134a cycles.

Hydrocarbons blends to R744 reduce T1 values, thus lower heat rejection on the gas cooler, reducing the exergy destruction. All R744 blends (HC's and ammonia) remarkable reduces P1 (lower operational pressure) comparing to R744 (100%), reducing the exergy destruction on the throttling valve. These blend characteristics allow to reduce the total exergy destruction.

Main findings are that improvements are possible in R744 transcritical cycles using blends to other natural refrigerants, considering 1st Thermodynamic Law, mass flow rate and lower operational pressure criteria, but not

according to 2nd Thermodynamic Law criterion. R744 and R717 are the most promising blends for future drop in experimental investigations.

6. ACKNOWLEDGMENTS

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