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Review Article

Assessment of the Use of Natural Refrigerants and Their Mixtures for Vehicle Air Conditioning: A Review Study

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ABSTRACT

Vehicle air conditioning is often blamed for its 20 to 40% overconsumption of fuel and its contribution to the greenhouse effect. This is largely due to the poor energy and environmental performances of the refrigerants used. Natural refrigerants as carbon dioxide (CO_2) or hydrocarbon (HC) can contribute to contain the problem. But Carbon dioxide, as a refrigerant, does not liquefy at the high pressure heat exchanger of the refrigeration loop within tropical outside temperature, due to its low critical temperature (31°C), and HC are flammable. An alternative solution appears to be the use of the mixture of carbon dioxide (CO_2) and hydrocarbon (HC) which is a less flammable or non-flammable refrigerant with low global warming potential. Thus the study reviewed the state of the art concerning the use of CO_2 for vehicle air conditioning and focused on mixtures of CO_2 and HC which are condensable at room temperature. The investigations were carried out on mixtures of CO_2 and HC with different molar fractions of CO_2 (from 0 to 100%). The equation of Van Poolen et al. made it possible to predict the critical points of the different mixtures. MATLAB software was used to compute the coordinates of the critical points of the mixtures and to deduce the eligible best mixtures candidate. The investigations showed that CO_2/R600a mixtures are more suitable for hot and tropical areas.

Key Words: Vehicle air conditioning, natural refrigerants, CO_2-HC mixtures, critical point, sustainable development

1. INTRODUCTION

Vehicle air conditioning (VAC) has become an important criterion when choosing a vehicle: thermal comfort and safety are sought by users. However, the automotive air conditioning system, through its leak tightness and the 20 to 40% overconsumption of fuel it generates, has a significant greenhouse effect on the environment. Nowadays, the main refrigerant used in automotive air conditioning is R134a, while Kigali's amendment prohibits the use of the latter from January 2019. Chemical industries propose the HFO-1234yf for its replacement, but it releases toxic products during its production and decomposition. It is also a flammable refrigerant. It is therefore urgent to find other alternatives. Both CO_2 and HC (propane, isobutane) are refrigerants of low GWP (Global Warming Potential). So they are potential candidates to achieve the objectives. The disadvantage of CO_2 is its low critical point inducing a transcritical refrigeration cycle with the need of a large heat exchanger at HP (High Pressure gas cooler) in warm and tropical areas. Thus the mixture of CO_2 of and HC, a promising technology, offers a less flammable refrigerant than hydrocarbons and requires a lower compressor discharge pressure than that of CO_2. Moreover, this technology avoids the risk of fire, and significantly reduces the fuel consumption of an air-conditioned vehicle, and therefore limits the emission of greenhouse effect gases. This work synthesized the state of the art and studied the variations in critical temperatures and critical pressures of different mixtures.

2. REVIEW OF LITERATURE

2.1. Inner comfort of a motor vehicle

A large focus was made on vehicle electrification in order to meet the demands of reducing fuel consumption and reducing greenhouse gas emissions. The construction of hybrid plug-in vehicles, and electric vehicles with very long autonomy, cooling the traction batteries during driving becomes a necessity to guarantee durability and an ultra-fast battery loading capacity. The cooling of the batteries is carried out via a water "chiller" which is a heat exchanger cooled with a water-antifreeze mixture or an evaporator connected to the air conditioning loop. Air conditioning loops with an evaporator and a chiller are already present on series vehicles such as the Tesla Model S or, more recently, the Volkswagen Golf GTE. The question raised as to what type of regulators to choose to obtain a good balancing of the loop with cooling capacity demands which can be very different between the two evaporators. While the first model is a long-range electric vehicle, the second is a plug-in hybrid whose battery has a much lower capacity. The cooling requirements are therefore not identical and justify the presence of a larger capacity chiller in the first case. In addition, while the chiller is supplied by a thermostatic expansion valve for this purely electric vehicle, a calibrated orifice ensures expansion of refrigerant in the second. No strategy known by the authors is present in the literature concerning the choice of the throttle valve for VAC. The impact of battery cooling using a chiller on the automotive air conditioning loop has been examined by simulation in the Dymola environment. [1] The results of the simulation pointed out the discomfort felt in the passenger compartment induced by the use of the "chiller" loop for different driving cycles, air climate conditions and refrigerants. However, the specialized literature did not reveal any reliable control strategy to address the problem.

Alexandrov et al. [2] proposed two- and three-dimensional CFD simulations (Computational Fluid Dynamics) to investigate the effect of various parameters such as car speed and outside temperature on the performance of mobile air conditioning systems. They simulated the flow in a vehicle and found a maximum temperature difference of about 7°C between two points in the car cabin. They concluded that problems such as areas with poor air circulation in the cabin can be resolved by a proper designing of air intake and outlet. The purpose of estimating the cooling and heating loads is to size a system capable of ensuring efficient thermal comfort for passengers whatever are the outside climatic conditions and the heat input in the vehicle. To do this, it is necessary to control the alternating cycle in order to maintain air quality by a comfort model. Optimization of the control has been studied for different operating conditions [3] and showed the difficulty of a control due to the non-linearity of the system. In the building sector, [21] the benefits of using a multi-evaporator air conditioning controller have already been proven. Although this type of decentralized model seems robust and applicable to the automobile, it requires the use of sensors and components currently too expensive and limited to a less restrictive environment than in the automobile field. However, a model of air conditioning consisting of two evaporators and a chiller [40] has been produced in order to assess the impact of various disturbances such as the opening of a valve or the change of the temperature set point. The advantage of an electronic expansion valve compared to a thermostatic one was studied. Khayyam et al. [4] gathered a set of models to calculate the different types of thermal loads encountered in a vehicle. For cars with a large passenger compartment volume or high-end vehicles with one or more rows of passengers, the presence of two evaporators is necessary to ensure thermal comfort up to the rear seats. A first modeling study of an air conditioning system with three evaporators (Figure 1) was carried out. [5] After validating their component models, an overhaul test during the first moments of air conditioning start-up was carried out to evaluate the performance of the air conditioning system. From a control point of view, a simple control of the proportional and integral regulation (PI) type on the temperature of the air blown to the rank1 evaporator was used to regulate the speed of the compressor. New technologies such as electronic valves and regulators (EXV) allow to adopt or envisage new control strategies. Selow et al. [6] have developed a virtual vehicle based on experimental correlations for each significant component of the vehicle. The virtual vehicle was divided into different modules, including the cabin

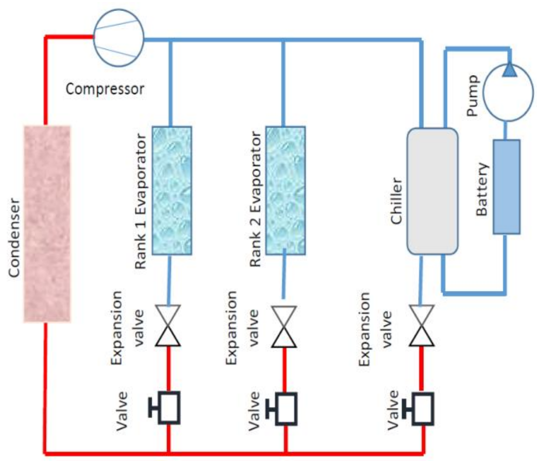

Figure 1: Schematic diagram of the multi-evaporator air conditioning loop [40]

climate. Such simultaneous operation of these modules could provide estimates without requiring heavy and costly experiments. In addition to the experimental tests, numerical simulations were also applied to improve the understanding of the AC load estimates. The methods proposed by ASHRAE and other organizations often consider the passengers compartment as a "global system" and do not take into account the three-dimensional distribution of temperature and flow parameters. To find exact solutions for the distribution of air flow, temperature, humidity, etc. is often challenging, but numerical methods provide good predictions. In the work of Bernard J. [7] air conditioning is carried out using aeronautical type equipment which uses only air as the refrigerant. The system has numerous favourable characteristics: a low mass and size, a high air speed allowing the adoption of small diameter distribution ducts and the possibility of bringing the compartments to its set-point temperature in a shorter time.

The function of the air conditioning system is to compensate the heat input of the vehicle for continuous changes in load in the cabin in order to maintain passengers in the required comfort zone. The Fanger thermal comfort model [8] has been widely used in AC research and applications as the basis for comfort assessment. Fanger et al. [9] have developed a model for calculating human thermal comfort specific to passenger cabins. When calculating the thermal load of a vehicle compartment, this model can be used to determine the corresponding thermal comfort state. The calculation of the cabin heat balance is a first key step in the design of suitable air conditioning systems. Particular care must be taken to it in order to optimize the related air conditioning system with a view to achieving good energy and environmental performance by avoiding excessive oversizing of equipments.

2.2. Energy performance of carbon dioxide

CO_2 or R744 is very cheap, it is used in the field of commercial, industrial and marine refrigeration and as an agent for extinguishing fires because it is non-flammable. It a refrigerant that provides a good coefficient of performance (COP), a very small pipe diameters and above all a GWP of one! However, CO_2 has a very low critical temperature close 31°C corresponding to a relatively high critical pressure (73.77 bar). [10] That characteristic makes more complex its use in hot ambient temperatures. In such cases, the refrigeration cycle becomes transcritical and the discharged gas can no more be condensed by the outside hot air, but can only be cooled down without phase change. Thus a large surface gas-cooler is required, operating under a very high pressure. Within hot ambient temperature, the COP of the refrigeration system decreases considerably. So, one stage refrigeration systems with CO_2 as a refrigerant are more suitable in cold climatic zones. [10]

Alexander Twinings was the first who proposed CO_2 as a refrigerant in an English patent filed in 1850. Karl Linde built the first CO_2 machine in 1881, the German Franz Windhausen improved this technology and he also received a patent in 1886. [11] Carbon dioxide, a refrigerant formerly used in industrial and maritime refrigeration, was proposed in 1990 by Professor Gustav Lorentzen as a replacement refrigerant, that year, he patented a CO_2 system operating according to a transcritical cycle where high pressure is controlled by the expansion valve. In 1992, he presented the experimental results of the first automotive air conditioning system operating with CO_2 following a transcritical cycle. [12] Laipradit et al. [13] carried out a simulation of a heat pump, the results show that the COP improves with the decrease in the temperature of the water at the inlet of the gas cooler. The decrease in inlet water temperature corresponds to a reduced refrigerant (CO2) temperature at the outlet of the gas cooler and therefore to a greater temperature difference between the inlet and outlet of the refrigerant at gas cooler level which explains the increase in COP. One of the experimental studies on heat pumps was carried out by Neksa et al. [14] The prototype included an intermediate exchanger. The evaporator pressure is 35 bar (corresponding to evaporator temperature of 0°C), and the gas cooler pressure is 90 bar. The system indicated a COP of 4.3 while heating the water from 8 ° C to 60 ° C. A simulation carried out by Robinson and Groll [15] showed an increase in COP of 7% when an intermediate exchanger was added to a basic transcritical system. The effects of an intermediate exchanger on the COP of a heat pump for heating water have also been checked by Kim et al. [16] Chen and de Gu [17] found that increasing the efficiency of the intermediate exchanger made the condensing pressure decrease and the COP to increase consequently. White et al. [18] used a theoretical model to compare the performance of a transcritical cycle system with exchanger compared to a basic system in which the surface of the gas cooler has been increased. Specifically, the surface area of the gas cooler has been increased equally to the area of the intercooler, this has increased the size of the gas cooler by 17%. That modification implied the increase of the optimum gas cooler pressure from 110 to 124 bar, which induced a 20% increase in heating capacity, although the COP remains unchanged. Fronk and Garimella [19] drew attention to the importance of the ratio of the heat transfer coefficients of CO_2 and the secondary fluid. Sarkar et al. [20] analysed the irreversibilities of the gas cooler and concluded that approximately 90% of the heat exchanger losses are due to the temperature differences between the refrigerant and the secondary fluid. The irreversibilities due to the pressure drop in the gas cooler were negligible in the study. Fronk and Garimella [21] have shown that in a counter-current gas cooler, the difference between the CO_2 outlet temperature and the secondary fluid inlet temperature (Δt_{min}) decreased compared to other fluids, the optimal pressure of the gas cooler also decreased. This leaded to a reduction in compressor work. Losses due to temperature difference can be reduced by increasing the heat transfer area, but there was a limit to the effectiveness of this approach. Theoretical optimization of the geometry of the concentric tube type heat exchanger was carried out by Sarkar et al. [22]

A cooling model gas emitter was developed by Dai et al., [23] this model was used to analyse the performance of the gas cooler in detail at different lubricating oil concentrations. The results showed that the oil has a dominant negative effect on the efficiency of the gas cooler, adding that the deterioration in performance becomes more evident if the operating pressure approaches the critical pressure and also that the decrease in performance is more pronounced for the higher mass flow rates. A mathematical model of finned tube gas coolers [24] where air is the secondary fluid has been developed and validated. The authors found that the power of the fan has a significant effect on the COP for high temperatures. Bendaoud et al. [25] developed a model to investigate the efficiency of finned tube evaporators. The model has shown that the pressure drop of CO_2 is smaller than that of other refrigerants. Yun et al. [26] used a numerical model to compare a micro-channel evaporator for air conditioning with a conventional evaporator. The model was validated with the results of an experimental system operating on R134a and also with the results of the study by Beaver et al. [27] The micro-channel evaporator has a greater heat transfer capacity (33%) than that of the conventional heat exchanger. Kim and Bullard [28] have developed a model to determine the performance of a micro-channel evaporator. The model has incorporated existing correlations for pressure drop and heat transfer coefficient, this model can be applied to facilitate the design of compact micro-channel evaporators. Jin et al. [29] have developed a model based on correlations developed specifically for CO_2. The model has been validated experimentally, this model is applicable for systems with a high vapour concentration or even superheated vapour. CO_2 is well suited for use with micro-channel tubes because its high operating pressure and high vapour concentration reduce the problem of poor phase distribution. Brix et al. [30] carried out a modeling study to analyse the effects of poor distribution, due to non-uniform air flow and also to the non-uniform phase distribution of CO_2 within the channels. For the horizontal flow of the refrigerant, the uneven distribution of the air flow and the vapour quality of the non-uniform refrigerant at the inlet of the evaporator caused the reduction of the evaporator capacity. For the upward vertical flow the poor air circulation distribution provoked the reduction in capacity, but the phase distribution of the refrigerant did not affect the capacity. The authors note that for a system with more than two channels the results may be different. The alignment and orientation of the evaporator plates also affect the performance of the CO_2 system. A simulation achieved by Yun et al. [26] compared the performance of two configurations of cross-flow evaporators with air. The study showed that the two plates arranged in a V shape give a better heat transfer capacity than the two plates arranged in series.

2.3. Energy performance of hydrocarbons (HC) Hydrocarbons are organic compounds which contain hydrogen and carbon. Hight hydrocarbons (propane or isobutane) are also very good refrigerants, the major disadvantage is that they are very flammable, explosive, and therefore dangerous. Chang et al. [30] studied the performance of a heat pump with different hydrocarbons (propane, isobutane, butane and propylene). Heat transfers were evaluated by measuring the average heat transfer coefficients on each portion. They showed that the heating and cooling capacities of a heat pump using R290 were slightly lower than those obtained with a hydro chlorofluorocarbon 22 (R22), but the coefficient of performance (COP) appeared higher. The cooling capacities delivered by the circuit with the hydrocarbon (R1270) were also higher than those offered by R22 and the COP showed significant improvement. Fernando and Palm [31] produced a prototype heat pump with a heating capacity of 5 kW with a low propane charge. The authors demonstrated its ability to operate with a light refrigerant load of 200 g within the outside temperatures of a Swedish climate, without reducing the COP. Park and Jung [32] studied the performance of a water / water heat pump using an R170 / R290 (ethane / propane) mixture. The R170 / R290 mixture had a compressor discharge temperature between 16.6 and 22.2 ° C lower than that of R22 under the same operating conditions. A decrease in the discharge temperature implies less thermal stress on the compressor and increases its life due to lower fatigue. Park et al. [33] carried out an experimental evaluation of a water / water heat pump using R433A (mixture of 30% propylene and 70% propane) as a retrofit refrigerant to R22. They used a compressor originally designed for the R22. The results showed that the COP of R433A was 4.9% to 7.6% higher than that with R22. Yu et al. [34] carried out the thermodynamic analysis of a transcritical cycle of a high temperature heat pump with an R32 / R290 mixture. They managed to produce domestic hot water at 90°. C. Corberán and Martinez [35] used a compressor with mineral oil and found that the amount of R290 refrigerant dissolved in the oil lubrication represented approximately 30% of the total load. Mineral oils are not expensive and are considered a good choice for high-capacity hydrocarbon applications located outside buildings (categories B - Supervised occupancy and C - Authorized occupancy) where the authorized load is higher. Ghoubali and Byme, [36] studied a heat pump for simultaneous heating and cooling with a heat output of 20 kW was developed with a load of 4 kg of propane. The choice of mineral oil was not a problem for the industrial partner. However, the use of mineral oil can cause a significant decrease in viscosity, which can be harmful to the compressor. Choudharia and Sapalib [36] (2016) made a comparative analysis of the performances of R290 and R22 on a standard vapour compression cycle for different evaporation temperatures at constant condensation temperature. It has been observed that the R290 gives a lower discharge temperature, which is an important factor in improving the service life of the compressor. The mass flow of refrigerant required with R290 is 50% lower than that of R22. The coefficient of performance of R290 closely matches that of R22. However, a higher COP can be expected if the equipments are optimized taking into account the specific properties of R290. In general, R290 is a better substitute for R22 in real applications because of its excellent environmental, thermo-physical and energy-efficient properties.

2.4. Properties of fluid mixtures The equation of state makes it possible to reproduce the thermodynamic properties of pure bodies and mixtures. Indeed, the famous Van der Waals equation of state proposed in 1873 has contributed a lot in the research of fluids properties. The use of increasingly efficient analytical expressions makes it possible to predict thermodynamic properties with good precision. In general, a state equation is initially developed for pure substances and it is written in the form: $f(P, V, X, T) = 0$. Where X represents the vector composition (molar fraction), and $X = 1$ for a pure body. Thanks to such equation of state, the specific volume, the enthalpy and the entropy of the refrigerant mixtures … can be performed, but the prediction of these properties is sometimes poor., so the appropriate choice of equations of state is crucial for better accuracy of the computed properties.

2.5. Automotive air conditioning system Figure 1 shows the main elements of the fluid circuit of an automotive air conditioning system.

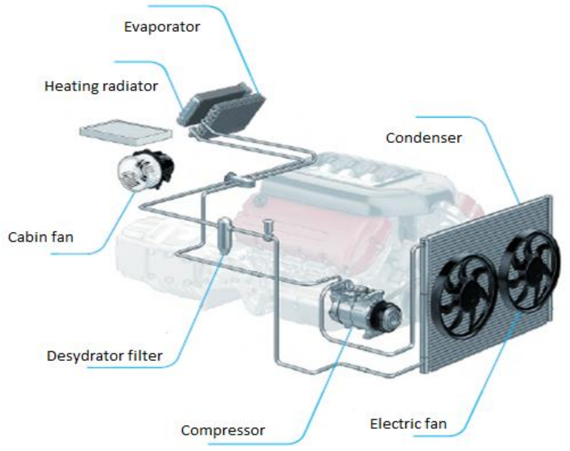

Figure 2: Vehicle air conditioning circuit loop [37]

3. PREDICTION OF THE CRITICAL POINTS OF THE CO_2 AND HC MIXTURE

The prediction of the critical points of a refrigerant mixture is a determining factor in the implementation of the thermodynamic properties of a refrigerant. With the mixtures of CO_2/HC. The point is to search for high critical temperature in order to build subcritical refrigerating loops to condensate vapour at the high pressure heat exchanger. This technology is efficient for tropical countries.

3.1. METHODS

3.1.1. Peng Robinson's equation

The model of Peng Robinson [38] is considered to be one of the best state equation models for predicting the thermodynamic properties of zeotropic binary mixtures. It's written:

$$P=\frac{RT}{v-b_i}-\frac{a_i(T)}{v(v+b_i)+b_i(v-b_i)} \qquad (1)$$

$$b_i = 0.0777960739\frac{RT_{Ci}}{P_{Ci}} \qquad (2)$$

$$a_i=0.457235529\frac{R^2T^2{}_{ci}}{P_{ci}}[1+m_i(1-\sqrt{\frac{T}{T_{ci}}})]^2 \qquad (3)$$

If $\omega_i \leq 0{,}491$, then $m_i = 0.37464+1.54226\omega_i -0.26992\omega_i{}^2$ (4)

Else $m_i = 0.379642+1.48503\omega_i - 0.164423\omega_i$ (5)

Where:

P: Pressure [Pa]
T: Temperature [K]
R: Universal constant of perfect gases [J / (mole.K)]
a_i (T): Temperature dependent function of the equation of state [K]
b_i : Covolume [m3]
v : Volume [m3]
P_{ci}: Critical pressure [Pa]
T_{ci} Critical temperature [K]
ω_i: Acentric factor -
x_i: Molar fraction of the liquid phase
α_{ij}: Fraction occupied by the group j in the molecule i.

3.1.2. Equation of Van Poolen et al

The equation of Van Poolen et al [39] is a correlation which allows to represent the curve of critical points. For this, it is necessary to carry out experimental measurements of few critical points (at least three points (Pc, xc)), to interpolate the coefficients of the following correlations:

$$T_{C_{mixture}}=x_1T_{C_1} +(1-x_1)T_{C_2}+G_{T_1}x_1(1-x_1) + \sum_{i=2}^{3}G_{T_i}x_i(1-x_1)(2x_1-1)^2 \; (6)$$

$$P_{C_{mixture}}=x_1P_{C_1} +(1-x_1)P_{C_2}+G_{P_1}x_1(1-x_1) + \sum_{i=2}^{3}G_{P_i}x_i(1-x_1)(2x_1-1)^2 \; (7$$

G_{Pi}: Correlation coefficient for critical pressure calculation
G_{Ti}: Correlation coefficient for critical temperature calculation

4. RESULTS AND DISCUSSION

Figure 3 shows the variation of the critical pressure of the mixtures as a function of the molar fractions of CO_2. It can be observed that when the molar fraction of CO_2 increases from 0 to 100%, the critical pressure of the CO_2 and R600a mixture increases from 38 bar to 73.825 bar and that of the CO_2 and R290 mixture increases from 44 bar to 73.825 bar. It should be noted that the CO_2 and R290 mixtures develop higher critical pressure than the CO_2 and R600a mixtures. Considering the critical point of R134a refrigerant, a former vehicle air conditioning refrigerant whose critical point is (Tc = 101.35 ° C, Pc = 40.7 bars), only the mixtures of CO_2 and R600a offer a possibility of a critical pressure close to the value of Pc = 40.7 bar.

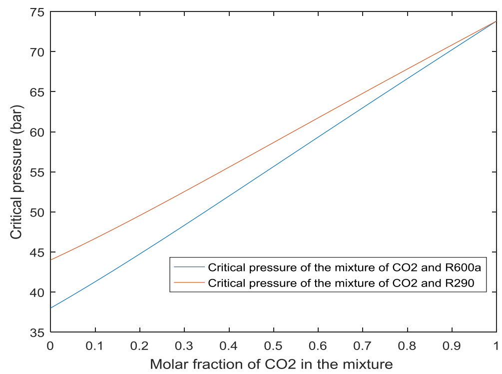

Figure 3: Evolution of the critical pressure of the CO_2 and HC mixtures as a function of the molar fraction

When the molar fraction of CO_2 increases from 0 to 1, the critical temperature of the CO_2 and R600a mixture decreases from 135.85 ° C to 31.0 ° C and that of the CO_2 and R290 mixture decreases from 97.85 ° C to 31, 0 ° C (Figure 4). It should be noted that the CO2 and R600a mixtures develop higher critical temperature than the CO_2 and R290 mixtures. Considering the critical point of R134a refrigerant, an old automotive air conditioning refrigerant which is (Tc = 101.35 ° C, Pc = 40.7 bars), only the mixtures of CO_2 and R600a show critical temperature close to Tc = 101.35 ° C.

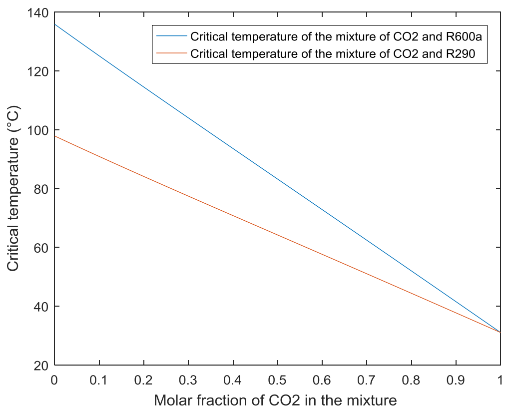

Figure 4: Evolution of the critical temperature of CO_2 and HC mixtures as a function of the molar fraction

Figure 5 shows the variation of the acentric factor (ω) of the mixtures as a function of the molar fractions of CO_2. When the molar fraction increases from 0 to 1, the acentric factor of the CO_2 and R600a mixtures decreases from 1.1810 to 0.2280 and that of the CO_2 and R290 mixtures decreases from 1.1520 to 0.2280. It should be noted that the CO_2 and R600a mixtures develop a slightly higher acentric factor than the CO_2 and R290 mixtures.

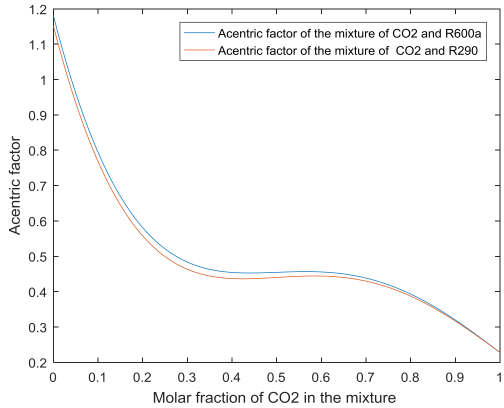

Figure 5: Evolution of the acentric factor of the CO2 and HC mixtures as a function of the molar fraction

5. CONCLUSION

In this study, an assessment of the state of the art on comfort in the passenger compartment of a motor vehicle, the energy performance of carbon dioxide (CO_2), hydrocarbons (HC), the properties of mixtures of fluids, the description of the automotive air conditioning system and the prediction of critical points for mixtures of CO_2 and R600a then CO_2 and R290 was developed. It has been pointed out that the CO_2 and R600a mixtures showed critical points close to that of R134a. These mixtures give the advantage of operating in two-phase. Next steps are the energy performance of these targeted mixtures.

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