

Università Politecnica delle Marche

Extended summary

Thermophysical Properties and Performances of Refrigerants with low environmental impact

Curriculum: Energetic

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Abstract

The activity of the PhD research focused on the study of thermophysical properties and performance of new refrigerants and their mixtures with low environmental impact. This study was carried out using three different experimental set-ups: the isochoric apparatus, the apparatus SLE and experimental refrigeration system operating with a cycle cascade.

The isochoric apparatus allows to find the P-V-T points of a gas or of a mixture both in the biphasic region and in superheated steam.

The use of two thermostatic bath with silicone oils with different viscosities allows to study a range of temperatures ranging from -50 ° C to 100 ° C.



It was immediately studied the new refrigerant R1234yf, which has replaced R134a in the car air conditioning, due to its low GWP value, in line with the new European directives.

Data weren't present in the literature yet, so results were published and subsequently confirmed by other studies.

We subsequently turned to the study of thermophysical properties of the mixture R1234yf-CO2, and then we tested the other isomer R1234ze and the mixture R1234ze-CO2.

The results were always compared with data from Refprop, the equation of Wagner in the biphasic region and the state equation of Martin-Hou in the region of superheated steam.

The charging system has undergone changes to decrease the uncertainty due to estimation of the lost mass, the weak point of isochoric apparatus.

A vacuum system was created to recover and weigh the loss mass in stages, so you can replace the previous estimate with a certain degree.

The plant has been repeatedly tested with known gases, in order to validate the tests performed.

The apparatus SLE allows to determine the melting point of the refrigerant gases and their mixtures, which were very low, requiring the use of liquid nitrogen.

First, we found the triple point of the following fluids:

- four hydro-olefin 2,3,3,3-tetrafluoroprop-1-ene, R1234yf, trans-1, 3,3,3
 tetrafluoropropene, R1234ze (E), 3,3,3-trifluoropropene, R1234zf, 1.2, 3,3,3 pentafluoropropene, R1225ye (Z);
- Five derivatives of propane-eptafluoropropano 1,1,1,2,3,3,3, R227ea; 1,1,1,3,3,3-exafluoropropano R236fa, 1,1,2,3,3,3 exafluoropropano R236ea, 1,1,2,2,3-Pentafluoropropane, R245ca, 1,1,1,3,3-Pentafluoropropane, R245fa;
- Three derivatives of the methane fluorometano, R41, and the Difluoromethane, R32, and the trifluoromethane, R23;
- The four derivatives of ethane pentafluoroethane R125, 1,1,1,2-Tetrafluoroethane, R134a, 1,1,1,-trifluoroethane, R143a, 1.1-difluoroethane, R152a;
- Mixtures: R1234yf-CO2, N2O and CO2-R1234ze + R41.



Regarding the latter, the results were adjusted, where necessary, by the method of Rossini and interpreted using the equation of Schröder.

The system was optimized by eliminating the internal copper coil that wrapped the measuring cell and placing the liquid nitrogen directly in contact with the measuring cell, thus improving heat transfer and reducing consumption of nitrogen liquid.

The charging system has been modified to decrease the uncertainty of the title in the case of mixtures. As well as for the isochoric apparatus a vacuum system was created in order to allow more shots to recover and weigh the lost mass.

Although this apparatus has been repeatedly tested with known gases in order to validate the tests.

Regarding the experimental refrigeration plant, we evaluated the performance of the refrigeration cycle cascade operating with CO2 and then with mixtures of CO2 + R23 in low temperature cycle.

For the control both of valve laminating and of heat load we have chosen to use PID control, which aims to simulate the behavior of a refrigerator for freezing food.

To improve the experimental plant, we used a volumetric flow meter on the high temperature cycle, after change of Labview software, which processes the data acquired from the plant, and we inserted a bypass system in the low temperature cycle; this system allows to recover the oil in circulation during the transition, in which the device operates in a partial load.

Keywords

Thermophysical properties, refrigerants, Solid-Liquid Equilibria, Isochoric Apparatus, cascade cycle

1 Problem statement and objectives

Chlorofluorocarbons (CFCs) have been phased out and Hydro-chlorofluorocarbons (HCFCs) will be phased out according to Montreal Protocol time frame in order to solve the depletion of the ozone layer problem. Hydrofluorocarbons (HFCs) could be the solution for new refrigerants, but they are greenhouse gases, hardly contributing to the climate change. To have a lower impact on the environment, the European Union decided to ban refrigerants with Global Warming Potential (GWP) of over 150 for 100 year time horizon in automobile air conditioning. This sector thus needs to find alternatives to the currently used fluid, R134a (GWP=1300 for a 100 yr time horizon). According to the new trends, the possible options in automobile air conditioning are natural refrigerants (i.e. carbon dioxide) and new synthetic refrigerants [1,2].

Although carbon dioxide has a GWP=1 and an Ozone Depletion Potential (ODP) that is zero, it has some restrictions due to its thermophysical properties. Besides, technical issues regarding the use of carbon dioxide in mobile air conditioning remain unresolved by the industry and the very high system pressures requires total redesign of just about every system component. For these reasons, CO_2 is probably not an ideal refrigerant for automobile air condition application.

DuPont and Honeywell recently developed a new refrigerant to replace R134a, a hydrofluoro-olefin called R1234yf (CF₃CF=CH₂, 2,3,3,3-Tetrafluoropropene). It offers similar thermophysical proprieties of R134a and for this reason requires minimum equipment changes. This fluid is mildly flammable, having a small gap between lower and upper flammability limits. It is also thermally stable with no significant corrosion to metals. It is a non-ozone-depleting substance, having an atmospheric lifetime of 11 days. It has also the lowest Life-Cycle Climate Performance (LCCP) compared to CO_2 and R134a. Its GWP is approximately 12 for a 20 yr time horizon and 4 for a 100 yr time horizon [3].

Regarding toxicity, the data demonstrate a low potential, similar to R-134a, by tests on male rats and mice [4]. Considering ATEL (Acute Toxicity Exposure Limit), R1234yf has also a favourable ATEL value (101000 ppm).

R1234yf thermodynamic properties are very similar to R134a: boiling point, critical point, and liquid and vapour density are comparable to R134a [5]. A complete comparison of the two fluids is also reported in table 1.

The Pressure-Volume-Temperature (P-V-T) properties of this fluid were measured both in the two phase and in the superheated vapour region by means on an isochoric apparatus [6], respectively. Searching for new perspective refrigerant mixtures for low temperature applications, isochoric measurements have been performed also for 2,3,3,3-Tetrafluoroprop-1-ene (CF₃CF=CH₂, R1234yf) + carbon dioxide (CO₂, R744) binary system, the other isomer R1234ze and the mixture R1234ze-CO2.

Data on triple point are important in the refrigerating industry, defining the lowest temperature limit at which the refrigerant may circulate in fluid state. In particular, for several refrigerants, triple point data present in the literature are extremely scarce or inaccurate

Solid-Liquid Equilibria (SLE) [7]. apparatus was used to measure the triple point temperature of 16 of the most widely applied alternative refrigerants, namely three methane derivatives (fluoromethane, R41; difluoromethane, R32 and trifluoromethane, R23), four ethane derivatives (pentafluoroethane, R125; 1,1,1,2-tetrafluoroethane, R134a; 1,1,1-



trifluoroethane, R143a; 1,1-difluoroethane, R152a), five propane derivatives (1,1,1,2,3,3,3-heptafluoropropane, R227ea; 1,1,2,3,3,3-hexafluoropropane, R236ea; 1,1,1,3,3-Pentafluoropropane, R245fa; 1,1,2,2,3-pentafluoropropane, R245ca and 1,1,1,3,3,3-hexafluoropropane, R236fa) and four hydro-olefines (2,3,3,3-tetrafluoroprop-1-ene, R1234yf; trans-1,3,3,3 tetrafluoropropene, R1234ze (E); 3,3,3-trifluoropropene, R1243zf and 1,2,3,3,3-pentafluoropropene, 1225ye (Z)).

Cascade systems appear to be promising for low-temperature applications; they consist of two separate refrigeration cycles, one working at a higher temperature and the other at a lower temperature. They are connected via an intermediate heat exchanger and its theoretical performance justifies experimental trials. This enables the high-temperature-circuit refrigerant (e.g. ammonia) to be confined to a proper machine room, while the safer low-temperature refrigerant is sent to evaporators around the factory. This is a very interesting application for the food industry, where temperatures between -18°C and -35°C are often needed [8].

The aim was to quantify the performance of a cascade refrigeration cycle using CO2 + R23 in the LTS and R404a in the HTS cycle. From the experimental data obtained an optimization procedure is performed using the Response Surface Methodology (RSM). Response surface methodology identifies the influence of each input variables to the output variables, which are, in this case, the coefficient of performance and the energy absorbed by the compressor at different working condition. The surfaces obtained are then used for a multi-objective optimization for the identification of those working conditions that maximize the coefficient of performance and the energy required by the compressors.

2 Research planning and activities

2.1 Isochoric Apparatus

Two twin thermostatic baths were filled with different silicone oils (Baysilone M10 and Baysilone M100, Bayer). After charging with the sample, the setup could be operated over two temperature ranges, approximately from (210 to 290) K and from (290 to 360) K, depending on which bath was used. The two silicone oils have different kinematic viscosity values (10 and 100 cSt at room temperature, respectively). The spherical cells and pressure transducer are immersed in one of the two thermostatic baths. An auxiliary thermostat was used to reach below-ambient temperatures. The cell volume was estimated to be (273.5 ± 0.3) cm3 at room temperature and the cell volume change with temperature was taken into account. A PID device was used to control the temperature, which was measured using a calibrated resistance thermometer. The charging procedure was performed by gravimetrical method.

The total uncertainty of the temperature measurements was ± 0.02 K. The uncertainty in the measurement of the mass inside the cell was estimated to amount to ± 5 mg. The volume of the cell, piping and pressure transducer cavity is measured with an uncertainty of ± 0.0003 dm³. From the uncertainties in the mass and volume measurements, the uncertainty in calculated molar volume was estimated to be always lower than ± 0.08 dm³·mol⁻¹.

The uncertainty in the pressure measurements stems from the uncertainty of the transducer and null indicator system, and the pressure gauges. The uncertainty of the digital



pressure indicator (Ruska, mod. 7000) is $\pm 0.003\%$ of its full scale. The total uncertainty in the pressure measurement, considering also the temperature fluctuations due to bath instability, was found to be always lower than $\pm 0.8\%$.

The charging procedure has been described elsewhere [9].



Figure 1. Schematic view of the experimental apparatus. Legend: (1): nitrogen reservoir, (2): vacuum pump (Vacuubrand, mod. RZ2), (3): precision pressure controller (Ruska, model 3981), (4): gas lubricated dead weight gage (Ruska, model 2465), (5): vibr. cylinder pressure gage (Ruska, model 6220), (6): digital temperature indicator (Corradi, RP 7000), (7): electronic null indicator (Ruska, model 2416), (8): stirrer, (9): heater, (10): cooling coil connected with an auxiliary bath, (11): differential press. transducer (Ruska, model 2413), (12): measurement chamber (VA), (13): expansion chamber (VB), (14): magnetic recirculating pump, (15): Pt resistance thermometer (Tersid, Pt 100), (16): vacuum pump for VB (Vacuubrand, model RZ2), (17): charging fluid reservoir, (18): Pt resistance thermometer (Hart Scientific, Pt 25) V1, V2, V3, V4 constant volume valves, (19): digital pressure indicator (Ruska, model 7000)

2.2 SLE Apparatus

The measuring cell, with a volume of approximately 47 cm3, was made out of a stainless steel cylinder with a cover welded to the body. The stirrer was kept in a perfectly vertical position by means of conical seats created on the raised bottom of the cell and on the underside of the cover so as to contain the rounded ends of the rod. The purpose of the stirrer was to prevent any premature stratification of the fluids comprising the various mixtures, while also assuring a greater homogeneity during the liquefaction and crystallization of the mixture. The stirrer inside the cell was turned by a magnet, which drives the plate welded onto the lower end of the rod. The magnet was housed in a seat made of brass, which was connected to the shaft of an electric engine driving the rotation of the magnet and thus also of the stirrer inside the cell. An absolute pressure transducer (HBM, mod. P8A) was installed in the charging tube.

A mass flow control was installed upstream from the dehumidifier: a needle valve with a shutter for adjusting the flow rate coming from the dry air supplier, as measured by means of the pressure difference read on a pressure gauge alongside it.



The airflow was also measured by a rotameter. The apparatus comprises a system for drawing the liquid nitrogen directly from its insulated tank with the aid of compressed air; the carrier fluid circulating in the circuit is thus the refrigerant fluid itself, instead of passing through an exchange with air.

To monitor the temperatures, the apparatus was equipped with one thermoresistance put in the measuring cell. The system parameters and the efficiency of the coil immersed in the liquid nitrogen were assessed using thermocouples at specific points on the copper tube. The platinum resistance thermometer used in the apparatus (100 Ω , Minco, mod. S7929) was calibrated by comparison with a 25 Ω platinum resistance thermometer (Hart Scientific, mod. 5680 SN1083).



Figure 2. Schematic illustration of the apparatus: 1 Measurement cell, 2 Stirrer, 3 Platinum resistance thermometer, 4 Pressure transducer, 5 Mass flow controller, 6 Dry air supplier, 7 Rotameter, 8 Liquid nitrogen tank, 9 Dewar containing the measurement cell, 10 Liquid nitrogen dewar manometer, 11 Nitrogen outlet, 12 External heating coil, 13 Charging bottle, 14 Vacuum pump system.

The operation of the system as a whole can be divided into two separate circuits and consequently two operating modes: a cooling system and a heating system.

When the system is used in the cooling mode, the compressed air (after passing through suitable dehumidifier filters) is delivered to the liquid nitrogen tank, which is thus placed under a positive pressure. Inside the tank, a PVC hose draws the refrigerant fluid from the bottom, which begins to flow through the circuit as soon as the pressure in the tank, controlled by a manometer , is sufficient to overcome the load losses produced by the circuit. After the first few moments, a steady state is reached and the liquid nitrogen flows through the circuit, rapidly cooling all of its surfaces to a very low temperature.

The refrigerant fluid passes first through the silicone capillary, then through the copper piping, exchanging heat with the measuring cell by evaporation as it moves through the coil, and finally flows out from the nitrogen outlet. In this cooling configuration, the nitrogen valve remains open and the heating circuit valve remains closed.

Conversely, when the system is operated in the heating mode, the dehumidified compressed air circuit is connected directly to the measuring cell's circuit and, in this case, the air acts as a carrier fluid and warms the cell, which is at a very low temperature by the



end of a measuring procedure. In this configuration, the nitrogen inlet valve remains closed. An external copper coil has also been provided: this can be heated by the operator to speed up the warming of the measuring cell.

2.3 Cascade System

The basic layout of the cascade refrigeration system considered is illustrated in Figure 1. This system is enbloc with a separate evaporator, installed in air treatment unit. The fluid in the HTS is R404A, while the low-temperature cycle was tested with R744.

The condenser in the HTS and the intermediate condenser/evaporator consist of shell and tube heat exchangers. The high temperature fluid flows in the copper tubes, while the low temperature condensing fluid flows in the shell.

The crossflow evaporator in the LTS comprises two copper tubes with fins distributed in 12 rows 32.5 mm apart. Each tube has $D_{int} = 11.3 \text{ mm}$, $D_{ext} = 12 \text{ mm}$, th = 0.35 mm, L = 24 m. The channel for the airflow is 35% smaller than the free cross-section because of the presence of the tubes. The heat exchanger surface area on the air side is 11.3 m2, including the surface area of the fins. The heat exchanger surface area on the refrigerating side is 1.7 m2. The evaporator is connected to an insulated chamber containing electrical heating elements, which are used to simulate the thermal load.

The test temperature inside the chamber is controlled by a PID, which regulates the thermal load of the electrical resistances in order to have a constant middle value of the temperature. Moreover, changing the value of the proportional parameter of the PID, we checked also the value of the thermal load.

A thermostatic throttle valve with a liquid liquid-charged bulb capable of operation between -40° C and $+10^{\circ}$ C and up to a pressure of 34 bar was used in HTS. For the LTS circuit we opted for an electronic thermostatic expansion controlled by a PID, and NTC temperature probe and a pressure sensor.

Two expansion tanks were included in the LTS circuit to reduce the pressure that would come to bear on the components during stoppages, in order to avoid the risk of exceeding the calibration pressures of the safety valves.

Temperature and pressure transducers were inserted along the circuit to study the cascade system. Temperature measurements were taken with copper-constantan T thermocouples inserted in copper pockets welded to the tubing. Moreover, the sump was flooded with silicone oil to prevent frost formation. The pressures were measured using piezoresistive pressure transducers and extensimeter transducers. The sensors were connected to a terminal block SCXI 1303 by National Instruments. In addition to recording temperatures, pressures and the power absorbed by the compressors, a data acquisition system was implemented using LABVIEW 7i. This data acquisition system can also calculate the enthalpies and flow rates, giving the cooling powers of the high- and low-temperature cycle, the coefficient of performance of the high and low-temperature cycle and of the system, the isentropic and volumetric efficiencies of the compressor in the HTS and LTS.

At system start-up, only the high-temperature cycle start working, while the low temperature cycle is enabled automatically when its pressure drops below a given threshold. When the low-temperature cycle cuts in, the hot gases are partially diverted through the expansion tanks in order to avoid the sudden rise in delivery pressure tripping the overpressure switch.





Figure 3. Basic layout of cascade system. 1. HTS Compressor; 2. HTS Condenser; 3. HTS Thermostatic valve; 4. Condenser\Evaporator; 5. HTS Liquid trap; 6. LTS Compressor; 7. LTS Manual valve; 8. LTS Evaporator; 9. LTS Liquid trap; 10. Regenerator; 11. Expansion tanks; 12. Test Chamber

The statistical techniques of RSM, is a useful tool for the identification and optimization of the variables that most influence a real process [10]. The generic relationship between a set of variables and defined response is reported in equation (1).

$$Y = f(x_1, x_2, \dots, x_i) + \mathcal{E}$$
⁽¹⁾

$$Y = b_o + \sum_{i=1}^n b_i * x_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} * x_i * x_j + \sum_{i=1}^n b_{ii} * x_{ii}$$
(2)

where Y represents the response and f represents the relationship between the response Y and the variables. The first step of the optimization procedure is the identification of the variables that most influence the cascade cycle. These variables are then correlated together using two different second-degree polynomial expression, as listed in equation (2), for the correlation of the experimental data with the coefficient of performance and the energy



absorbed by the compressors. Starting from the response surface obtained a constrained multi-objective optimization is performed, for the identification of those configurations that guarantee the minimization of the energy adsorbed and the maximization of the coefficient of performance. The multi-objective optimization is performed using the evolutionary algorithm NSGA-II [11]. NSGA-II can identify a Pareto frontier with efficiency, is a fast and elitist multi-objective evolutionary algorithm, which tasks a sorting of the individuals of a given population, according to the level of non-domination. This methodology uses an approach based on elitism and preserving, where the elitism consists in storing all the non-dominated solutions found so far, beginning from the initial design. This elitism enhances the convergence properties towards the best Pareto array. NSGA-II adopts a mechanism of parameter-less diversity preservation where the spread of solutions is guaranteed even without sharing parameters. In fact, diversity in the spread is maintained by a sharing function method, used to assign fitness to each individual. This means that the algorithm uses the crowding distance, in order to estimate the density of solution, and the crowded comparison operator, to obtain a uniformly spread Pareto frontier. NSGA-II allows both continuous ("real-coded"), and discrete ("binary- coded") design variables, which have respectively a Base equal to 0 and a Base equal to a positive integer. Thus, it provides the decision maker with a complete illustration of the optimal solution space.

3 Analysis and discussion of main results

3.1 Isochoric Apparatus

The summary of the measurements, both for the saturation (black circle symbol) and superheated vapor region (other symbols) of the new refrigerant R1234yf is reported in figure 4.



Figure 4. Summary of the isochoric measurements of R1234yf. ○, m=1.367 g; □, m=1.629 g; ◇, m=2.621 g; △, m=5.893 g; ▽, m=6.669 g; ▲, m=7.481 g; +, m=10.518 g; ■, m=12.327 g; ◆, m=23.602 g; -, m=37.550 g; ★, m=39.663 g; ●, m=124.890 g.

About vapour pressure data, measurements were carried out in a wide temperature range, from (224 to 373) K, and at pressures from (39 to 3716) kPa. A total of 35 experimental points were obtained. Data in the saturation vapour region were compared with REFPROP 8.0 prediction [12], with a preliminary equation developed with these data [9]. Again producing much higher deviations, the datum close to the critical point (T) 365.93 K and (P) 3218.4 kPa was not considered in the equation of state fitting



procedure. In terms of absolute deviations, almost all of the experimental data were found to be within ± 1 kPa; in terms of relative deviations, data are consistently within ± 0.1 % with just five points well within ± 0.5 %, as reported in Figure 5-6.

Experimental data were also fit to the four parameter Wagner equation:

$$\ln \frac{P}{P_c} = \frac{T_c}{T} [A_1 \tau + A_2 \tau^{1.5} + A_2 \tau^3 + A_4 \tau^6]$$
(3)

where $\tau = (T_c - T)/T_c$; the critical temperature $T_{c=}368.15$ K [4].

During the fitting procedure, the critical pressure was fitted as a parameter and the best results were obtained with $P_c = 3389.5$ kPa, a value close to $P_c = 3404$ kPa reported by the prelimary equation of state [12][13] and quite far from $P_c = 3240$ kPa [14]. The following values were found for the parameters : A₁ = -7.82239, A₂ = - 2.15165, A₃ = -21.16155 and A₄ = -26.25422.

Defining the deviation in pressure as

$$dP = \frac{1}{n} \sum_{\substack{i=1\\ n}}^{n} [(P_{\exp} - P_{calc}) / P_{\exp}] \cdot 100$$
(4)

$$\left| dP \right| = \frac{1}{n} \sum_{i=1}^{n} \left[\left| (P_{\exp} - P_{calc}) / P_{\exp} \right| \right] \cdot 100$$
(5)

where *n* is the number of experimental points. The following values were found: dP = 0.004 % and abs(dP) > 0.11 %. The error distribution is shown in Figures 7-8. The absolute deviations were found to be well distributed, excluding one point, within ± 1 kPa, while the relative deviations were found to be usually within $\pm 0.25 \%$ and always within $\pm 0.5 \%$.



Figure 5. Scatter diagram of the saturated pressure-absolute deviations between experimental pressures (P_{exp}) and pressures calculated from REFPROP 8.0 (P_{calc}).





Figure 6. Scatter diagram of the saturated pressure-relative deviations between experimental pressures (P_{exp}) and pressures calculated from REFPROP 8.0 (P_{calc}).



Figure 7. Scatter diagram of the saturated pressure-absolute deviations between experimental pressures (P_{exp}) and pressures calculated from the fit with the Wagner equation, equation (3) (P_{calc}) .



Figure 8. Scatter diagram of the saturated pressure-relative deviations between experimental pressures (P_{exp}) and pressures calculated from the fit with the Wagner equation, equation (3) (P_{calc}) .



Superheated vapour data were obtained along 12 isochores and a total of 136 point were obtained.

Since no experimental data were available in the open literature, our experimental results were also compared with the preliminary equation of state [12,15] developed at NIST and reported in Figures 9-10. Deviations showed an AAD(P) = 0.34 %.



Figure 9. Scatter diagram of absolute pressure deviations produced from Refprop 8.0 for R1234yf. Symbols are denoted as in figure 5.



Figure 10. Scatter diagram of relative pressure deviations produced from Refprop 8.0 for R1234yf. the dashed line represents the experimental uncertainty. Symbols are denoted as in figure 5.

The experimental P-V-T measurements were also fitted with the Martin Hou equation of state in its original expression [13]:

$$P = \frac{RT}{(v-b)} + \frac{A_2 + B_2 + C_2 e^{-5.475\frac{T}{T_c}}}{(v-b)^2} + \frac{A_3 + B_3T + C_3 e^{-5.475\frac{T}{T_c}}}{(v-b)^3} + \frac{A_4}{(v-b)^4} + \frac{B_5}{(v-b)^5}$$
(6)

where



$b = V_c - \frac{\beta V_c}{15 \cdot Z_c}$	(7)
P , V	

$$Z_c = \frac{T_c - V_c}{R \cdot T_c} \tag{8}$$

$$\beta = 20.533 \cdot Z_c - 31.883 \cdot Z_c^2 \tag{9}$$

$$T' = T_c \cdot (0.9869 - 0.675 \cdot T_c) \tag{10}$$

The Martin-Hou EoS was regressed minimizing the AAD (P) and acting on two parameters: m = (P-P)/(T-T) and T_B , the Boyle Temperature. According to the original paper [10], T_B spanned from 500 to 1000 K, while the *m* value spanned from 0.1 to 0.9, taking as a reference the values obtained from the critical isometric estimated by REFPROP 8.0 [8]. All the obtained parameters were summarized in Table 1.

Table 1. Parameters for the Martin-Hou EoS.

T_{c}	367.95
P_c	33.451764
V_c	238.58074
Z_c	0.26433
m	0.752018
β	3.1998139681293
T _{Bovle}	551.66
T	0.808450374220908
b	46.0405839810452
R	82.0574587
A_2	-28999357.5820942
B_2	48775.0064774891
C_2	29307214.3135024
A_3	4787634452.67778
B_3	-7552243.72827284
C_3	-5642815560.71898
A_4	-181061886091.117
B_5	18047800638.0284

In order to minimize the AAD(P), the 1 plus 1 Evolution Strategy technique [14] based on the evolutionary fast algorithm was developed.

Comparing equation (6) with the experimental temperature and volume data, the deviations from the experimental pressure were calculated for each data point and the results are shown in figures 11 and 12. Deviations showed an AAD(P) = 0.44 %.





Figure 11. Scatter diagram of absolute pressure deviations produced from Eq. (4) for R1234yf. Symbols are denoted as in figure 5.



Figure 12. Scatter diagram of relative pressure deviations produced from Eq. (4) for C The dashed line represents the experimental uncertainty. Symbols are denoted as in figure 5.

Results compared with REFPROP 8.0 prediction were well within the experimental uncertainty (calculated to be always lower than 0.8 %), while few points of the results compared with the Martin Hou EoS were out of the experimental uncertainty limit, shown with the dashed line. However, both predictions, excluding 2 series, generally showed the same trend of deviations for the different isochores.

In addition, the isochores with lower charge showed a slight increase, in absolute value, of deviation with the lowering of temperatures.

Regarding R1234yf+CO₂ binary system, the experiment covered both two phase and superheated vapor regions and were been performed within a temperature range that spans from 223 to 373 K and within a pressure range from 160 to 1700 kPa.





Figure 13. Summary of the isochoric measurements of R1234yf+CO₂ binary system

3.2 SLE Apparatus

The results of the temperature data acquisitions were corrected using the Rossini method because a constant cooling rate is not indispensable and was not guaranteed by our experimental method.

This is a graphic method that considers the area contained by the tangent to the curve in the descending stretch after the temperature drop, and curve itself; then a vertical segment (a) is taken, which divides the area into two equal parts; then a second, horizontal segment (b) is obtained, from the point of intersection between the segment (a) and the tangent to the curve, up until it identifies the temperature corresponding to this new point on the axis of the ordinates (T_m) .





The entity of the corrections takes into account the fact that the fluid is still in a liquid state during the metastable state (supercooling) that precedes proper solidification. In table 2 we have the results of measurements.

Fluid	Sample purity	T _{lit}	Source	T_{I}	T_2
CO_2	99.99 %	216.58	Angus et al. 1976	216.6	216.5
N ₂ O	99.99 %	182.34	Calado et al., 1986; Fonseca et al., 1989	182.0	181.7
DME	99.8 %	131.65	Ihmels and Lemmon, 2007 Stull et al., 1969	131.6	131.6
R23	99.6 %	118.02	Magee and Duarte-Garza, 2000	117.7	117.0
R32	99.98 %	136.34	Luddeke and Magee, 1996	137.1	135.7
R41	99.9 %	129.82	Magee, 1997	129.8	129.8
R125	99.96 %	172.52	Luddeke and Magee, 1996	173.0	172.5
R134a	99.98 %	169.85	Tillner-Roth and Baehr, 1994	169.7	169.8
R143a	99.9 %	161.34	Magee, 1998	161.4	161.4
R152a	99.94 %	154.30	Blanke and Weiss, 1992; Magee, 1998	154.3	154.3
R227ea	99.7 %	146.35	Beyerlein et al., 1993	-	145.9
R236ea	99.99 %	127.05	Beyerlein et al., 1993	-	126.6
R236fa	99.94 %	178.95	Beyerlein et al., 1993	-	179.8
R245ca	99.9 %	199.75	Beyerlein et al., 1993	-	196.0
R245fa	99.97 %	171.05	Beyerlein et al., 1993	-	170.0
R1234yf	99.9 %	122.77	Minor and Spatz, 2008	123.45	122.6
R1234ze (E)	99.9 %	168.62	Lemmon et al., 2011	-	168.8
R1243zf	99.9 %	-	-	-	122.8
R1225ye (Z)	99.9 %	-	-	-	134.3

Table 2. T_1 =values obtained by a thermoresistence; T_2 : values obtained by a thermocouple

3.3 Cascade System

When the system starts, normally the temperature inside the chamber was higher than the checked one by PID controller. Only when the temperature reaches this value, the



thermal load started in order to balance the cooling power of the low temperature cycle and to stabilize the average value of the temperature. The setting values of the temperature were -20 °C, -24°C, -25°C, -30°C, -40°C varying also the thermal load from 1.37 kW to 3.35 kW.

We charged the system with 2.00 kg of R744 in the LTS and 4.00 kg of R404A in the HTS. Problems relating to the achievement of high working and transient pressures obliged us to close partially the compressor's intake valve in LTS. Progressively reducing the evaporating pressure, we gradually reopened the valve. The experimental results obtained are listed in table 2.

Starting from the experimental results obtained, and defined like variables that reported in table 3, except for the COP and P_{ABS} ; the regression coefficients were calculated. After the regression coefficients were obtained, the estimated responses could be easily calculated. The capacities of estimation of these two surfaces are tested using the equation (11), and the results obtained for each response are reported in figure 15.

$$AD = |\frac{Y_{EXP} - Y_{CALC}}{Y_{EXP}}| * 100$$
(11)

EXP	$T_{\rm EV}$	T _{C-HTS}	SH _{LTS}	SH _{LTS}	T _{C-LTS}	T_{EV}	СО	P _{ABS}
ID	LTS [°C]	[°C]	[°C]	[°C]	[°C]	HTS [°C]	Р	[kW]
1	-44.16	53.19	8.53	7.81	-9.60	-12.59	1.23	5.92
2	-43.73	53.66	7.98	7.88	-9.18	-12.28	1.25	5.96
3	-43.93	53.41	8.93	7.56	-9.51	-12.56	1.23	5.93
4	-43.47	54.19	8.51	7.89	-8.78	-11.87	1.24	6.04
5	-39.87	54.52	14.66	7.86	-10.09	-12.68	1.07	5.85
6	-39.21	54.46	13.51	7.87	-10.20	-12.73	1.08	5.87
7	-38.58	52.61	13.99	7.42	-11.92	-14.75	1.10	5.62
8	-38.62	52.20	14.11	7.27	-12.33	-15.32	1.12	5.57
9	-44.49	53.97	7.14	7.79	-10.17	-12.83	1.02	5.85
10	-44.96	53.94	7.60	7.86	-10.21	-12.76	1.02	5.84
11	-45.03	53.35	7.89	7.68	-10.69	-13.49	1.02	5.76
12	-45.31	53.53	6.65	7.81	-10.65	-13.20	1.02	5.79
13	-47.20	49.02	9.30	8.23	-14.01	-16.57	1.12	5.25
14	-47.36	49.42	8.13	7.85	-13.39	-16.47	1.11	5.34
15	-46.07	50.22	8.31	7.91	-12.80	-15.53	1.10	5.45
16	-45.65	50.43	7.25	8.01	-12.56	-15.42	1.10	5.49
17	-49.84	46.87	6.80	6.78	-16.76	-20.00	1.05	4.96
18	-51.43	46.03	5.61	7.95	-18.34	-20.84	1.08	4.78
19	-51.41	46.18	3.23	7.42	-18.12	-20.81	1.09	4.82
20	-51.80	45.58	5.26	7.97	-18.79	-21.24	1.08	4.72
21	-51.71	45.48	3.39	6.91	-18.76	-21.52	1.06	4.74
22	-50.88	48.88	5.89	7.34	-16.39	-19.22	1.45	5.07
23	-50.83	49.72	2.23	6.08	-15.47	-18.57	1.44	5.16

Table 3. Operating points with CO2 as the fluid in the LTS



Author (Name and surname) <i>Title of the PhD thesis</i>							
-51.77	42.94	4.78	7.53	-19.93	-22.53		
-51.34	43.75	2.02	7.35	-18.89	-21.98		
-51.42	43.62	5.05	7.77	-19.45	-21.84		
-51.00	44.08	2.16	7.26	-18.53	-21.60		
-52.64	42.14	0.67	6.73	-20.21	-23.92		
-52.77	41.79	0.46	6.63	-20.56	-24.27		

6.73

6.64

7.25

7.18

7.12

7.11

7.73

7.30

7.24

7.33

-20.15

-20.36

-20.65

-19.62

-19.64

-19.37

-12.55

-13.56

-16.47

-17.65

-23.85

-24.13

-23.27

-22.51

-22.33

-22.18

-14.90

-16.38

-20.04

-20.99

0.86

0.56

1.42

0.29

0.50

-0.14

16.55

16.20

3.46

2.52

1.29

1.28

1.33

1.29

1.12

1.13

1.13

1.13

1.20

1.20

1.20

1.20

0.88

0.93

1.05

1.04

4.64

4.77

4.69

4.80

4.59

4.56

4.61

4.57

4.60

4.67

4.69

4.73

5.59

5.51

5.17

5.05



Figure 15. Response surface methodology absolute deviations

The average deviations for each response are very low and below the 0.8 % for the COP and below the 0.1 % for the P_{abs} . Starting from these two surfaces is possible to start the optimization procedure, using the evolutionary algorithm NSGA-II.

The outcome of optimization is a set of solutions representing the Pareto frontier (Ghosh and Tsutsui,), witch is given in Fig 16. With this Pareto frontier is possible to identify that configurations with the best compromise between the maximization of COP and minimization of the energy absorbed by the compressors.



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-52.48

-52.66

-53.01

-52.55

-52.44

-52.35

-41.44

-41.86

-45.81

-47.82

42.19

41.95

43.23

43.99

44.09

44.27

54.81

52.38

46.59

45.51



The configurations identified with the best compromise between COP minimization and energy absorbed is reported in table 4.

Table 4. Working parameters of the optimized configuration

T _{EV-LTS} [°C]	T_{C-HTS} [°C]	SH _{LTS} [°C]	SH _{HTS} [°C]	T _{C-LTS} [°C]	T_{EV-HTS} [°C]
-49.8	49	9	7	-10	-17.4
СОР		1.25	P _{ABS} [kW]		4

4 Conclusions

The P-V-T measured data confirmed that R1234yf is very similar to R134a in terms of vapor pressure: a discrepancy of about 15 kPa at low temperatures (at about 243 K) and of -20 kPa at high temperatures (at about 352 K) was evident. This confirms that the fluid under investigation could be a valuable option in automobile air conditioning.

The triple point and the Pressure-Volume-Temperature (P-V-T) properties of R1234yf were measured by means of Solid-liquid equilibria and isochoric apparata.

The properties of this fluid were measured both in the two phase and in the superheated vapour region. Data were collected in a temperature range from 224 to 373 K.

The experimental data were compared with a preliminary equation of state developed also with present data. Results were generally within the experimental uncertainty limit.

The measured triple-point data for the refrigerants revealed a generally good agreement with the literature, excluding few fluids that revealed some discrepancy.

Based on a series of experimental test performed on a cascade cycle an optimization procedure is been proposed. The optimization procedure was based on the identification of two different response surface methodologies, required to describe the relationship among the variables, relative to the cascade cycle, and the coefficient of performance and the electrical energy absorbed by the compressors. From these two surfaces, using NSGA-II algorithm, a multi-objective optimization is performed. From the optimization is possible to identify configurations of the variables that guarantee the minimization of the energy absorbed and the maximization of the coefficient of performance of the cycle.



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