

TERNARY ZEOTROPIC MIXTURE WITH CO₂ COMPONENT FOR R-22 HEAT PUMP APPLICATION

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ABSTRACT

The paper presents results of a simulation and laboratory study of the performance of a zeotropic mixture R-744/32/134a in a water-heating heat pump. The goal of the research was to obtain operating parameters comparable to a system charged with R-22. The performance of R-22 served as a reference for the ternary mixture studied.

A semi-theoretical simulation model was used first to examine the influence of R-744 properties on the mixture performance and to determine the optimum mixture composition. The formulated mixture, R-744/32/134a (7/31/62) was then tested in a laboratory. The experimental apparatus consisted of a counter-flow condenser and evaporator. The primary measurement of capacity was performed on the heat-transfer fluid side. Compressor power was obtained from speed and torque measurements on the open compressor's shaft. Compared with the performance of R-22, the COP of R-744/32/134a was better by 9.5% at a 21% increase in volumetric capacity.

1. INTRODUCTION

The objective of this research project was to demonstrate a successful operation of a high efficiency heat pump employing a zeotropic mixture with a zero ozone-depletion and a small greenhouse warming potentials (ODP and GWP, respectively). The project addresses the technical challenges resulting from international agreements regulating the use of ozone-depleting substances. The signatory countries of the Montreal Protocol agreed to phase out production of chlorine-containing refrigerants with deadlines depending on the ODP of the fluids [1]. A search for a proper substitute has to consider factors such as capacity, efficiency, flammability, oil/refrigerant solubility, toxicity, etc. [2, 3]. This study investigated possible R-22 alternatives with the goal of achieving a comparable system capacity and 10% improvement in Coefficient of Performance (COP). The tests were performed in COCH (Refrigerating Machinery Research Center in Cracow, Poland).

Nomenclature

COP	-	Coefficient of Performance
M	-	torque [N m]
n	-	compressor RPM
P_{comp}	-	compressor power [kW]
p	-	pressure [kPa]
Q_{vol}	-	volumetric heating capacity [kJ/m ³]

Q	-	heating capacity [kW]
RPM	-	compressor speed - revolutions per minute
T_{glide}	-	refrigerant temperature difference [K]
T_{in}	-	water inlet temperature [°C]
T_{out}	-	water outlet temperature [°C]
T	-	water temperature difference [K]
V	-	water volumetric flow rate [l/min]
HTF	-	heat-transfer fluid

2. DESCRIPTION OF TEST FACILITY

The test facility, shown in Figure 1, was designed and constructed to allow on-line comparison of an R-22 heat pump with a heat pump charged with an alternative refrigerant. The rig consisted of two identical heat pump systems connected to the same heat-sink and heat-source loops for maintaining operating conditions. The compressors had a nominal refrigeration capacity of 11.5 kW (for R-22) and were equipped with electric motors of a nominal electric power of 7.5 kW. The evaporators and condensers had a tube-in-tube counterflow configuration to facilitate temperature glide matching between the refrigerant and HTFs. Both heat exchanger types consisted of ten sections made with 2.5m long copper tubes; however, other tube dimensions were different. For the evaporators, the external tube was 42mm x 1.5mm (external diameter x wall thickness) and internal pipe was 28mm x 1.5mm. For the condensers, the external tube was 35mm x 1.5mm and the internal tube was 22mm x 1mm. Water was used as the heat-transfer fluid (HTF). All heat exchangers were properly insulated.

The following control and safety devices were installed to ensure proper and reliable operation of the experimental rig:

- electronic expansion valve to control vapor superheat at the evaporator outlet at different operating conditions
- electrically-heated thermostatic water tanks equipped with power control and mixing pumps for stabilizing temperature of the water supplied to the evaporators and condensers
- frequency transducers for controlling each compressor's speed
- all required safety devices for each compressor
- safety temperature sensors at the water outlet of each heat exchanger to guard against water freezing in the evaporator and excessively high temperature in the condenser.

The control system was designed to allow both manual and microprocessor control of the experimental rig. The data acquisition system was based on a personal computer with PC-add on cards and multiplexers installed. The system collected data from:

- 106 temperature measurement points (thermocouples)
- 10 pressure measurement points (pressure transducers)
- 4 water flow measurement points (two turbines and two electromagnetic meters)
- 2 liquid refrigerant mass flow measurement points
- 2 compressor power inlet measurement points (watt-hour meters)
- 1 torque meter for torque and RPM reading.

In addition to measurements recorded on the data acquisition system, refrigerant and water temperatures along condenser and evaporator were displayed on separate displays located on the test rig. Water inlet and outlet temperatures were simultaneously measured by a data log system working independently of the basic data acquisition system.

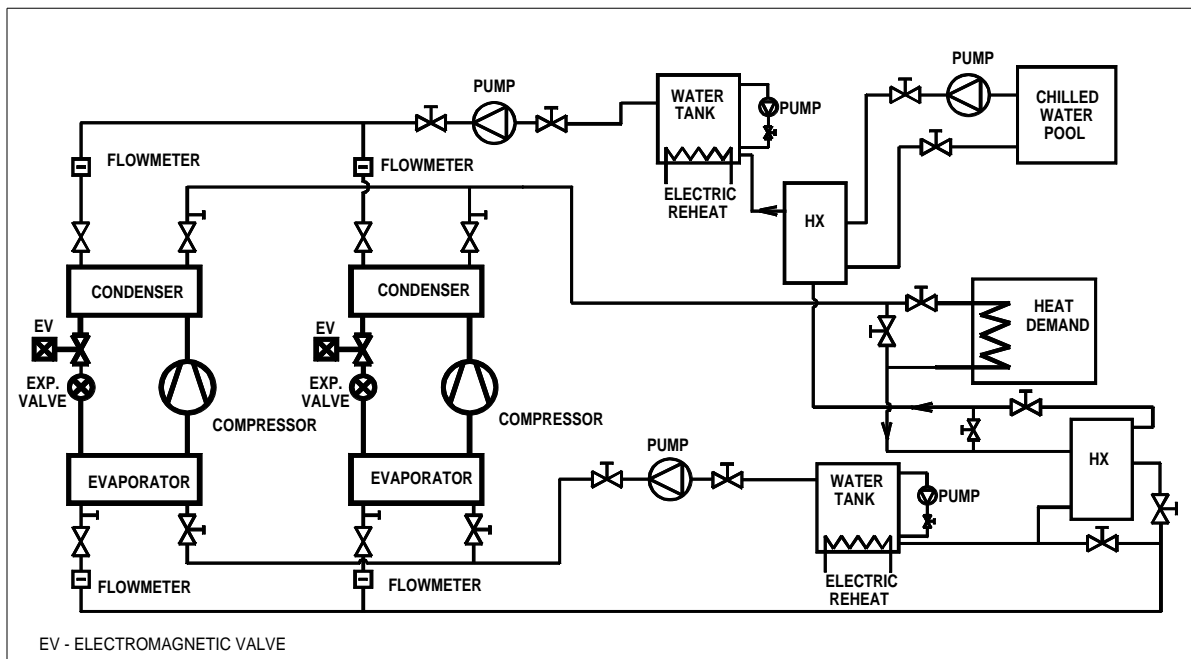


Fig. 1. A schematic layout of test facility

3. TEST PROCEDURE

Cycle simulations using a semi-theoretical model, CYCLE-11 [4], preceded laboratory tests. The goal of these simulations was to derive an optimum mixture (i.e., mixture components and their mass fractions) for use in the laboratory test program. Eight fluids were considered as possible mixture components: R-123, R-124, R-152a, R-134a, R-290, R-32, R-125, and R-744 [5, 6, 7]. A mixture of R-744, R-32 and R-134a showed the most promising results and, consequently, was prepared for testing. The tests included R-22 and R-32/134a as a reference. Table 1 shows selected properties of the tested fluids obtained from REFPROP [8].

Table 1. Selected properties of the tested fluids

Refrigerant	Mass Fraction (%)	Molar Mass [g/mol]	$T_{\text{glide}}^{(1)}$ [K]	$Q_{\text{vol}}^{(2)}$ [kJ/m ³]	Liquid ⁽³⁾ Thermal Conductivity [W/(m K)]	Liquid ⁽³⁾ Viscosity [μP]
R-22	100	86.47	0	4020.4	0.09671	2194
R-32/134a	29/71	79.79	6.7	3843.1	0.1129	2290
R-744/32/134a	7/31/62	73.39	17.1	4869.6	0.1178	2157

- (1) $T_{\text{dew point}} - T_{\text{bubble point}}$ at saturation pressure corresponding to $T_{\text{dew point}} = 0 \text{ }^\circ\text{C}$
 (2) Calculated for average $T_{\text{evaporator}} = 2.5 \text{ }^\circ\text{C}$ and $T_{\text{condenser}} = 52.5 \text{ }^\circ\text{C}$
 (3) Saturated liquid at pressure corresponding to $T_{\text{dew point}} = 0 \text{ }^\circ\text{C}$

Table 2. Complete range of operating conditions (HTF temperatures)

Evaporator		Condenser	
$T_{\text{in}} \text{ [}^\circ\text{C]}$	$T \text{ [K]}$	$T_{\text{in}} \text{ [}^\circ\text{C]}$	$T \text{ [K]}$
20	10	35	15
			20
		40	15
			20
		45	15
			20
	15	35	15
			20
		40	15
			20
45	15		
	20		

where:

- T_{in} - water inlet temperature
 T - water temperature change in the heat exchanger

The complete project involved an extensive test program shown in Table 2 in terms of operating temperatures of the HTFs. This paper focuses on the results obtained for the water-heating applications, which is indicated in Table 2 by the entries made in a bold font. As shown in the table, the tests were performed at the specified temperatures of water at the inlet and outlet of the condenser and the evaporator. The water temperatures were controlled within $\pm 0.2 \text{ K}$. Refrigerant superheat at the evaporator outlet and subcooling at the condenser outlet were set to

5 K \pm 0.2 K. The test program included six compressor speeds from 1000 RPM to 1500 RPM at a 100 RPM step (see Table 3). Although initial tests were performed using both compressors, the final tests (reported here) used the compressor equipped with the torque meter. This eliminated the influence of changing electric motor efficiency with the load, and allowed the compressor power to be obtained from torque and RPM readings provided by the torque meter. The reported system capacities are the water-side capacities obtained from measurements of a water mass flow rate and water temperature difference between condenser inlet and outlet. The mineral oil supplied with the compressor was used during R-22 tests. This oil was replaced with a polyolester oil for experiments with the binary and ternary mixture. No hardware changes were made between different tests except a filter-dryer. The mixture composition was measured by means of gas chromatograph. The samples were taken simultaneously from the liquid line and the compressor discharge line. The measurements were repeated several times for each mixture tested. Table 4 presents relative uncertainties of the basic measurements and the compounded uncertainties for capacity, compressor power and COP.

Table 3. Operating conditions for tests with different compressor speed

evaporator T_{in}/T_{out} [°C]	condenser T_{in}/T_{out} [°C]	superheat [K]	subcooling [K]	compressor speed [RPM]
20/5	35/50	5	5	1000-1500 (step 100)

Table 4. Relative uncertainties (%) of the measurements (approx. 95% confidence level)

T	V	M	n	p	P_{comp}	Q	COP
1.6	0.5	0.2	0.2	0.13	1.2	1.7	2.1

4. RESULTS

The obtained test data for the water heating application provided the basis for comparison of the refrigerants using two methods: drop-in evaluation and constant-capacity evaluation.

Drop-in Comparison

The tests were run at 1500 compressor RPM to perform a drop-in comparison. In these tests refrigerant charge and the opening of the expansion valve were adjusted to obtain the same evaporator superheat and condenser subcooling (5 K). Table 5 presents the obtained heating capacity and COP. The mixtures performed better than R-22, both in terms of capacity and COP. The capacity increase over that of R-22 was 2.9% for R-32/134a and 18.6% for R-744/32/134a. For COP, the increases were 3.9% and 2.5% for the binary and ternary mixture, respectively.

The significant 18.6% increase in capacity achieved by the R-744/32/134a mixture is related to its higher evaporator pressure (Table 6). While pressures for R-22 and R-32/134a were similar, 496 kPa and 498 kPa in the evaporator and 1959 kPa and 2099 kPa in the condenser, those for the R-744/32/134a mixture were higher, 571 kPa and 2680 kPa in the evaporator and the condenser, respectively. Pressure drops in both evaporator and condenser were small for all the fluids (approximately 15-20 kPa).

Table 5. Heating capacities and COPs for tests with 1500 compressor RPM

mixture	Q [kW]	$\frac{Q - Q_{R-22}}{Q_{R-22}} \cdot 100\%$ [%]	COP	$\frac{COP - COP_{R-22}}{COP_{R-22}} \cdot 100\%$ [%]
R-32/134a (29/71)	17.7	2.9	3.801	3.9
R-744/32/134a (7/31/62)	20.4	18.6	3.750	2.5

Table 6. Refrigerant pressures at different compressor speeds

Fluid	Compressor speed [RPM]	Evaporator outlet [kPa]	Condenser inlet [kPa]
R-22	1500	496	1959
R-32/134a	1500	498	2099
R-744/32/134a	1500	571	2680
R-32/134a	1448	498	2095
R-744/32/134a	1185	585	2514

Constant-Capacity Comparison

Since R-22 showed a lower heating capacity than the two mixtures studied, the R-22 heating capacity at 1500 compressor RPM was selected as a target capacity for the constant-capacity comparison. This allowed the use of the test data of R-22 at 1500 compressor RPM directly. To obtain the mixtures' COPs for the same capacity level, the mixtures' measured data were correlated as a function of compressor speed, and used these correlations for calculating performance at the compressor speeds that resulted in the capacity match. Figures 3 and 4 show this process graphically for R-744/32/134a, for which the capacity match with Q_{R-22} occurred at 1185 RPM. In these figures, the solid lines were generated by linear fits to the test data. For comparison, the figures include simulated performance, dotted lines predicted by CYCLE-11. The solid and dotted lines do not overlap; however, they show a similar trend validating CYCLE-11 as a useful support tool for a laboratory effort.

Table 7 shows compressor speeds and COPs for the mixtures for the constant-capacity comparison. The 1448 RPM indicated for R-32/134a means a 3.5% reduction of the required compressor displacement. The additional benefit measured for R32/134a is its COP that exceeded that for R-22 by 5.2%. For the R-744/32/134a mixture, the reduction of RPM was more considerable, down to 1185 RPM, which corresponds to a 21% reduction of the

compressor displacement required to match the capacity of R-22. The COP of R-744/32/134a was the highest of the fluids tested, exceeding that of R-22 by 9.5%. The high COP of R-744/32/134a was achieved because of several factors. The glide-matching of the HTF and zeotropic mixtures was probably the most influential one. Figure 2 presents the glides of the HTF and refrigerant along heat exchanger sections. Other favorable factors were good transport properties and low molar heat capacity. The latter promotes good COP in the basic refrigeration cycle. Although no flammability tests were performed, it may be expected that the R-744/32/134a mixture is not flammable. This speculation is based on the fact that the R-32/134a (30/70) mixture is marginally flammable, and bracketing the flammable component, R-32, by non-flammable R-744 and R-134a may render this ternary mixture to be safer.

Table 7. Compressor speeds and COPs for constant-capacity evaluation

mixture	RPM	$\frac{COP - COP_{R-22}}{COP_{R-22}} \cdot 100\%$ [%]
R-32/134a (29/71)	1448	5.2
R-744/32/134a (7/31/62)	1185	9.5

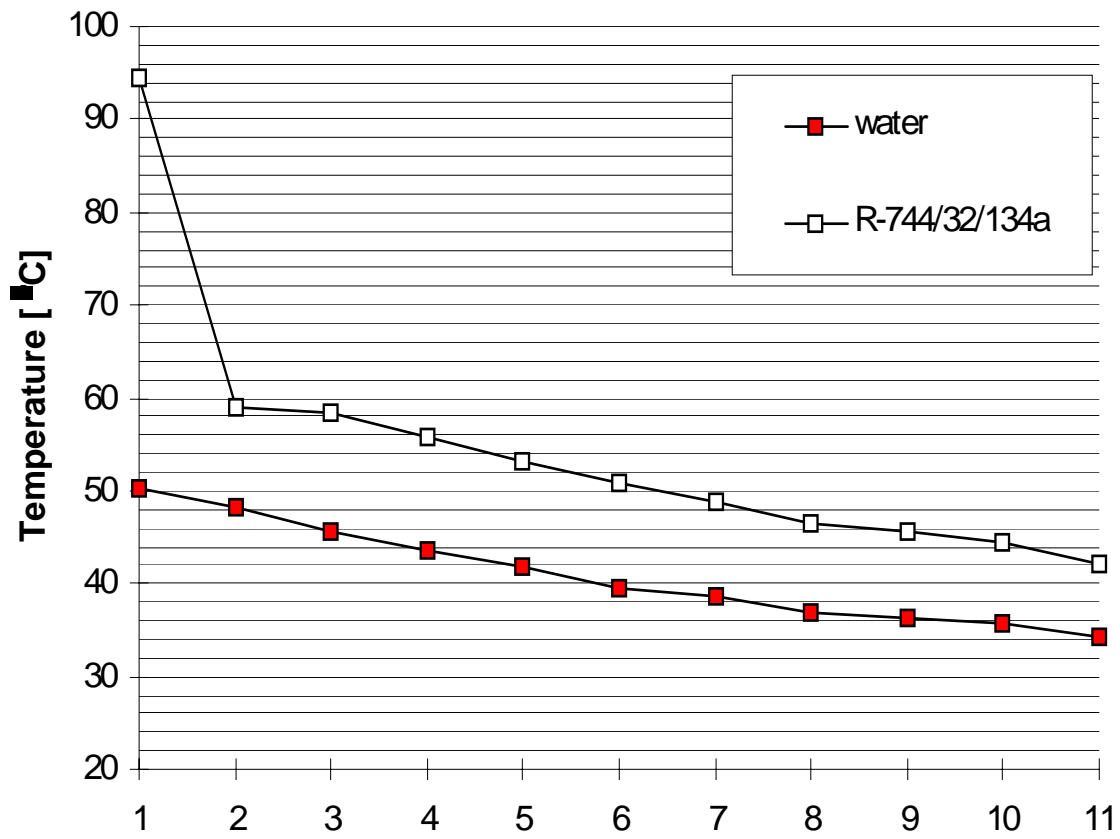


Fig. 2. Temperature glide along condenser sections for R-744/32/134a and water

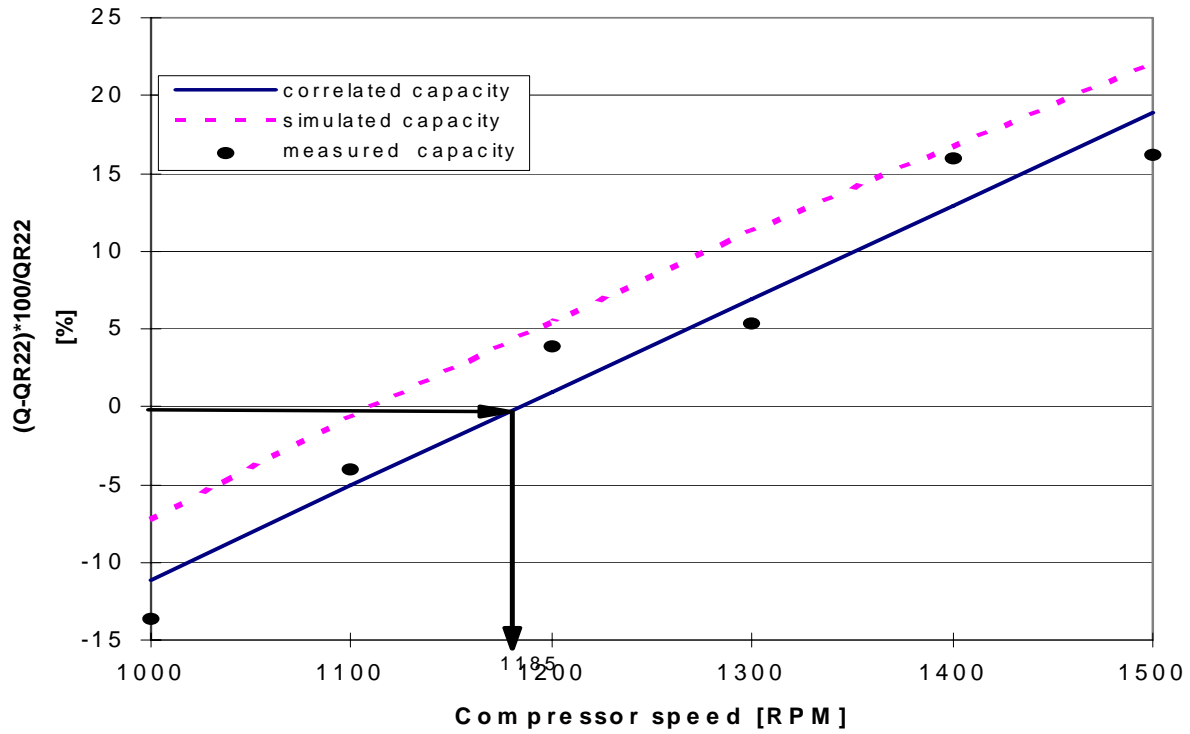


Fig. 3. Heating capacity of R-744/32/134a at different compressor speeds referenced to heating capacity of R-22 at 1500 compressor RPM

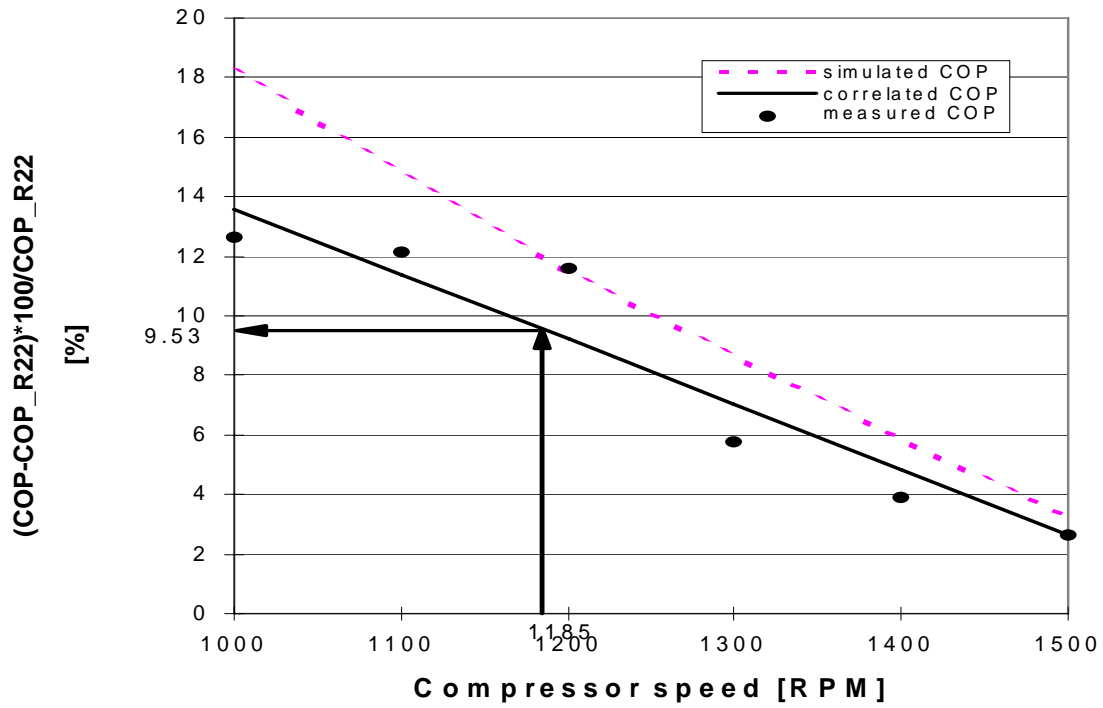


Fig. 4. COP of R-744/32/134a at different compressor speeds referenced to COP of R-22 at 1500 compressor RPM

5. CONCLUSIONS

1. Employing CO₂ as a third component to binary mixture R-32/134a caused an increase of system heating capacity and an increase of COP.
2. Ternary mixture R-744/32/134a (7/31/62) is applicable as "drop-in" replacement of R-22 only for low temperature heat pumps because of its excessive condensing pressure.
3. The mixture R-744/32/134a (7/31/62) seems to be very promising as an R-22 substitute in newly designed refrigerating/heat pumping systems. The experimental COP increase in comparison with R-22 reached almost 10% for a system using counter-flow heat exchangers.

6. REFERENCES

- [1] Bivens D.B. and D.A. Didion - "The Role of Refrigerant Mixtures as Alternative CFCs", Proceedings of ASHRAE's 1989 CFC Technology Conference, 1989
- [2] Kruse H. - "European Research Concerning CFC and HCFC Substitution", Int. Journal of Refrigeration, vol.17, no. 3, 1994
- [3] Nakatani K., Ikoma R.K. and I.Yosida, "Development of High Temperature Heat Pump Using Alternative Mixtures", Proceedings of ASHRAE - Purdue CFC Conference, July 1990, Purdue University, U.S.A.
- [4] Doma ski P.A. , Mc Linden M.O. "A simplified cycle simulation model for the performance rating of refrigerants and refrigerant mixtures" - Int. Journal of Refrigeration, 1992, vol. 15, no. 2
- [5] Garofano A. Fabberti V. - "Theoretical comparison on refrigerant cycle for air conditioning system operating with R22, R134a blends and relative experimental tests" - 'CFC's The Day After", II Conf. B1/2, E1/2, Padova, Italy, 1994
- [6] Hesse U, Kruse H - "Alternatives for CFC's and HCFC's based on CO₂" - IIR Commission B1/2, Ghent, Belgium, 1993
- [7] Lorentzen G. - "Large Heat Pumps Using CO₂ Refrigerant" - IIR Commission B1/2, Ghent, Belgium, 1993
- [8] Huber M., Gallagher J., McLinden M., Morrison G., "NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP), Version 5.0 ", National Institute of Standards and Technology, Gaithersburg, MD USA, 1996

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