SOME ALTERNATIVES OF REFRIGERANTS TO BE USED IN MOBILE AIR CONDITIONING SYSTEM

João Bosco Coelho , bosco@ifma.edu.br
Antonio Remi Kieling Hoffmann , remi@ifma.edu.br
Federal Institute of Maranhão, Imperatriz Campus – Imperatriz – MA – Brazil

Enio Pedone Bandarra Filho, bandarra@mecanica.ufu.br
Faculty of Mechanical Engineering – Federal University of Uberlandia, Av. Joao Naves de Avila, 2121 – Uberlandia–MG–Brazil

Abstract. *Halogenated compounds used as refrigerants cause significant environmental impacts, putting in dangerous the life on earth and therefore must be replaced. The chemical refrigerants HFO and HFO-1234yf or the HFO-1234ze with ozone depletion potential of zero and low GWP are strong candidates to work with refrigeration and heat pump. On the other hand the natural refrigerant* CO_2 *also with zero ODP and low GWP is a safe solution because it is not flammable or toxic and it is friendly to the environment. This article highlights the basic thermo-physical and transport properties of HFO-1234yf of HFO-1234ze and* CO_2*, from available experimental data. It also discusses the adequacy of* CO_2 *in air conditioning systems for high temperature environments, to improve their energy efficiency. The thermo-physical and transport properties of* CO_2 *are better than those of chemical refrigerants in other environments, a result of the compact size of the system which leads to greater efficiency in most conditions. Thus there is no doubt more* CO_2 *refrigeration systems will be seen in the future.*

Keywords: *MAC, Air Conditioning System, HFO-1234yf,* CO_2*, R-134a.*

1. INTRODUCTION

The use of vehicles equipped with air conditioning system has become a common practice. This equipment assures passengers thermal comfort and it also helps on defrosting car glasses. It contributes, thereby, with the driving conditions besides enhances security.

The evolution of air conditioner refrigerants can be observed throughout the history. Initially, refrigerants such as ammonia and carbon dioxide were used. Later, they were replaced by CFC: simpler on use, exhibiting higher chemical stability and apparently lack of environment risks. But, due to its potential to destroy the Ozone Layer, it was also substituted, this time, by HCFC, which had a lower Ozone depletion potential. Currently, HFC-134a is widely used. It is not an ozone depleting substance (Zero ODP), otherwise, it has a high global warming potential (GWP of 1430).

The synthetic refrigerant fluids CFC and HFC have been suffering from actions against their use on the last two decades, due to their destructive environmental effects. Initially, because of its Ozone Depletion Potential, and later, due to its Global Warming Potential.

Their replacement by an environmentally friendly refrigerant can take place with the use of a natural product or a HFC similar substance (with low contribution to global warming). The favorite candidate, which demonstrates better performance, is in Carbon Dioxide. Among the synthetics, HFO-1234yf is a promising one.

The carbon dioxide viability has been already proven and it makes this substance the better alternative between the natural refrigerant fluids. It is neither toxic nor flammable, has high volumetric capacity and excellent heat transfer properties. This substance also exhibits good characteristics for reverse cycle (heat pumps), however, CO_2 heat pumps operate in a so-called transcritical cycle and, due to the elevated system pressures, some components require different configuration. Another important aspect is its reduced efficiency while operating in hot climates, such as Dubai and Phoenix.

According to the HFO-1234yf manufacturers, this substance is considered the ideal substitute due to its similar chemical and physiochemical properties compared to HFC-134a. Besides, it exhibits low toxicity level and it is not an ozone depleting substance. It also has a low global warming potential, attributed to its short atmospheric cycle. In the other hand, in the environment, this gas decomposes in Trifluoroacetic acid (TFA). This substance do not suffer breakdown processes, accumulating in the nature until achieve harmful levels. Its hazard potential is still unknown, but TFA, among other, can exhibit mutagenic and teratogenic effects, impairment of fertility and, certainly will reach natural water sources.

It is widely know that Industry searches for a solution with low GWP and high energy efficiency. And lots of interests are involved in this subject. This paper presents thermal and physics properties of HFO-1234yf and Carbon Dioxide. These are the probable fluids to be used in mobile air conditioning system in the next years.

2. REFRIGERANTS OF THE NEXT-GENERATION

The Kyoto Protocol is an international instrument aimed at reducing the emission of gases that contribute to the greenhouse effect and consequently the global warming process.

HFC-134a currently used in air automotive conditioning systems is a fluoride compound which has considerable global warming potential (GWP of 1430) and thus is considered one of the greenhouse gases. Its direct and indirect emissions tend to enhance due to the significant increase in vehicle amount and in the number of air conditioning systems on the world vehicle fleet. This growth requires the development of new technologies, as well as the emergence of alternative refrigerants.

For many years, Industry has been searching for a suitable refrigerant to replace HFC-134a, which is the only refrigerant fluid approved by all manufacturers of automotive air conditioning in the World. The alternatives has been intensified by the 2006 European Directive decision which states, from January 2011, that the GWP of a refrigerant used in air conditioning system should not exceed 150, for all new types of vehicles launched in European Union market. The HFC-134a GWP is on a well above level compared to what has been established, justifying the need for its replacement by an alternative substance.

Among the natural alternative refrigerants, Carbon dioxide (CO_2) has the most favorable environmental parameters. It is neither toxic nor flammable, has a GWP of 1, against 1430 of the HFC-134a, and has already fully developed technology. It is also important the fact that is not necessary to capture the emitted CO_2 during the air conditioning system charging or repairing, and at the end of life cycle, which simplifies the handling and leads to some economy, (Antonijevic, 2007). It had already been used as a refrigerant at the beginning of the last century, despite of its non-appropriate thermal and physical properties. Since 1940, Carbon dioxide has been replaced by chemical refrigerants, which exhibit good capacity of cooling systems operating with very low pressure, and therefore, being easier to use. In the late 1990's Carbon Dioxide reappeared, mainly due to its favorable environment characteristics.

Regarding synthetic refrigerants, for refrigeration work and for the heat pump cycle, two refrigerant types are in focus: HFO-1234yf and HFO-1234ze, both with zero ozone depletion potential. They also have low global warming potential, HFO-1234yf has GWP of 4 and 6 for the HFO-1234ze. It is not easy to find reliable information on thermal, physical or transport properties of these substances. They have short lifetimes in the troposphere and this is a good reason to be considered as candidates for next-generation refrigerants. However, they can affect the atmospheric environment for the generation of photochemical oxidants in the troposphere, due to their reactivity with OH radicals. Moreover, it is known that the HFO-1234yf decomposes in the environment to form the trifluoroacetic acid (TFA) which may cause ecological damage. Besides some technical issues, it is the formation of TFA, the environmental risk that it implies and its flammable property, the major obstacles to the use of this refrigerant, (Dalang, 2010).

The fluid HFC-152a can be considered a transition, since this fluid is produced commercially. However, the use of this refrigerant needs some special care and must be use in combined cycle, since this refrigerant is flammable. The suggestion is to use two loops, the refrigerant R-152a loop isolated of the automobileŠs cabin and water or ethylene glycol as secondary fluid inside of the cabin. Some authors found a better performance of the R-152a in comparison with the R-134a.

Kim et al. (2008) conducted an experimental study comparing the R-134a and R-152a in single stage system. The results showed a better performance of the R-152a in relation to the R-134a, for the same compressor velocity, the COP for the R-152a was higher between 30 to 42% and the refrigeration capacity for the R-152a presented values between 20 and 41% higher than obtained for the R-134a.

3. CO_2 PROPERTIES AS REFRIGERANT

Quite a few general properties of CO_2 are absolutely ideal for the use of this product as a working fluid in vapour compression refrigerating machines and heat pumps, (Cavallini, 2010 *apud* LORENTZEN 1994):

- carbon dioxide is available in the environment, waste of many technological processes; its cost is thus extremely low, easily available anywhere, and its recovery from dismissed equipment or in maintenance is not required;
- being a natural fluid, its harmlessness to the biosphere is demonstrated, both as far as known actions are concerned in the immediate (as the depletion of stratospheric ozone), and with reference to possible still unknown harmful actions (an always possible danger in the use of new synthesised products foreign to nature, as the happenings with CFCs and the pesticide DDT have shown). CO_2 is certainly a greenhouse gas, but for its possible use as a refrigerant one recurs to recovery from industrial waste. For this application therefore the added greenhouse impact is to be considered nil, as nil is of course its impact on the stratospheric ozone depletion;
- it is a product that displays no special local safety problem, as it is non-flammable and non-toxic. CO_2 is heavier than air and it can accumulate in the lower part of a nonventilated ambient, especially in a basement, causing suffocation for lack of oxygen. Holds of ships may be prone to this kind of events;

- it is an inert product, compatible with all common materials encountered in a refrigerating circuit, both metals and plastics or elastomers.

The property that decisively defines behavior of CO_2 in a refrigeration cycle is its low critical temperature (31.1 °C). Hence vapor compression cycle with CO_2 at ambient temperatures works usually partly above the critical point and at much higher pressures than R134a cycle operated by the same temperature levels (Fig. 1). Consequently, the process of heat rejection is not any more predominately condensation, but transcritical vapor cooling with significant gaseous refrigerant temperature decrease inside 'gas cooler' heat exchanger, (Antonijevic, 2008).

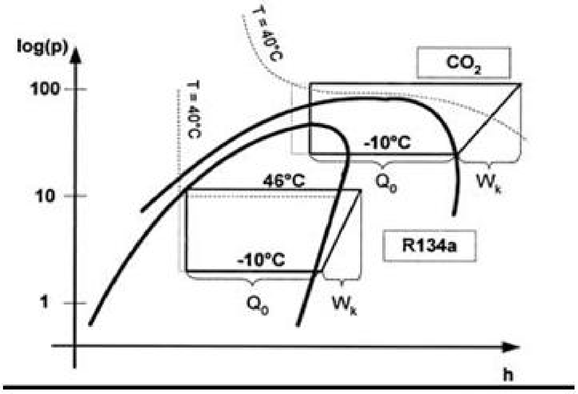

Figure 1. Typical cooling cycles of R134a and CO_2 in pressure-enthalpy diagram. Antonijevic (2007).

The refrigerant properties are important for the concept of refrigeration system and its components. Key aspects of CO_2 properties as refrigerant have been discussed in publications, for example, Nekså (2002) and Kim et al. (2004). The properties of CO_2 are well known and Tab. 1 shows that they are quite different from other conventional refrigerants, (Antonijevic, 2008).

Table 1. Characteristic properties of Carbon Dioxide and some other traditional refrigerants

Fluid	Critical Temperature [°C]	Critical Presssure [bar]	Saturation pressure at -20°C [bar]	Volumetric Latent Heat at -20 °C [kj/m^3]$^{(1)}$	Molecular Mass [kg/kmol]
CO_2	31.06	73.84	19.67	14592	44.01
R-22	96.15	49.90	2.453	2371	86.47
R-134a	101.06	40.59	1.327	1444	102.03
R-410A	71.36	49.03	4.007$^{(2)}$	3756	72.59
NH3	132.25	113.33	1.901	2131	17.03

$^{(1)}$: latent heat divided by the specific volume of saturated vapour. $^{(2)}$: refers to the liquid phase

The operation close to the critical point leads to three distinct features of CO_2 systems when used as the only refrigerant, (Nekså et al., 2010).

- **Heat is rejected at supercritical pressure when the heat sink temperature is high**.

  The system will then use a transcritical cycle that operates partly below and partly above the critical pressure. The high-side pressure in a transcritical system is determined by refrigerant charge and not by saturation pressure. The system design thus must consider the need for controlling the high-side pressure to ensure a high COP and capacity. A refrigerant buffer volume is needed in order to enable charge variations, but since no liquid can be stored at the supercritical pressure, other options must be found. The most common is to buffer liquid on the low pressure side of the system or at intermediate pressure.

- **The pressure level in the systems will be relatively high, often between 30 and 120 bar**.

  The high operating pressure results in a high volumetric capacity. This is leading to smaller required cross sectional flow areas in the system and thus also smaller inner volume of the system. As a consequence, components should be redesigned to fit the properties of CO_2. The advantage is that components most often can be designed more compact since e.g. the compressor displacement needed for a given capacity compared with HFC-134a is 80-90% smaller. Further, compressor pressure ratios are low, thus giving favourable conditions for achieving high compressor efficiency. The relatively high operating pressures in evaporators and condensers/gascoolers also lead to very efficient heat transfer compared with HFCs, further enabling heat exchangers to be of a more compact design. Higher pressures are often associated with a higher hazard, but due to smaller volumes of piping and components, the stored explosion energy in a CO_2 system is not much different from that of a conventional system.

- **Large glide in temperature of the refrigerant during heat rejection**.

  At supercritical or near-critical pressure, all or most of the heat transfer from the refrigerant takes place by cooling dense single phase gas. The heat rejecting heat exchanger is therefore called a gascooler instead of a condenser. Since heat is transferred as sensible heat, the temperature will be gliding according to the actual high pressure. Gliding temperature can be an advantage in heat pumps for heating water or air. For other applications care must be taken in order to achieve as low refrigerant temperature as possible out of the gascooler. With proper heat exchanger design the refrigerant can be cooled to less than or a few degrees above the entering coolant (air, water) temperature, and this improves the COP of the systems compared to if typical temperature approach assumptions from simple cycle comparison approaches are used. It should be noted that provided the gas cooler outlet temperature can be cooled to a sufficiently low temperature, the COP will be higher than in a typical HFC system. Internal heat exchange to subcool high pressure gas with the compressor suction gas may also improve efficiency, especially at high ambient temperatures.

Due to differences in thermodynamic properties of CO_2 and the cycle characteristics compared to HFC-134a, Fig. 2 illustrates the CO2 highest efficiency at low room temperatures, while systems using HFC-134a are lightly more efficient at higher room temperatures.

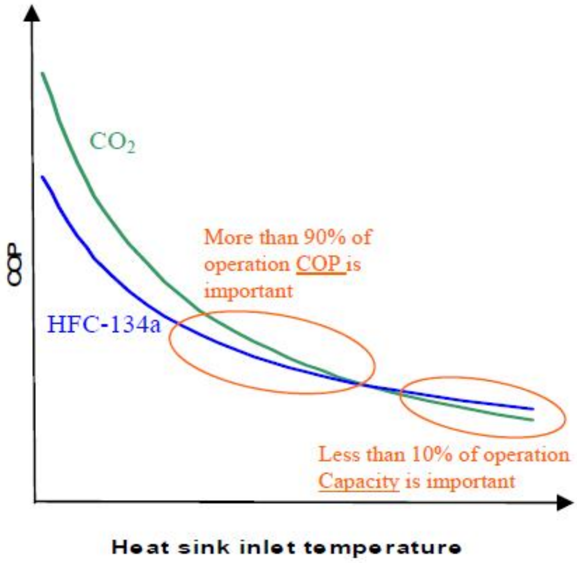

Figure 2. Typical COP vs condenser/gascooler inlet temperature of heat sink. Nekså (2010).

Seeing that working pressure levels in R744 system are much higher than in R134a system, usually in the range 3-11 MPa all the components need to be designed in the novel way to withstand and benefit from the higher pressure. Material strength as well as the wall thickness at CO_2 - air boundaries must be increased, (Antonijevic, 2007).

At present level of CO_2 air conditioning system development fuel consumption, for the given system performance, is already lower than with R134a system.

4. PERFORMANCE AND ENERGY CONSUMPTION

Air conditioning systems based on CO_2 are already on par with systems using R-134a in terms of performance and power consumption. In some cars already manufactured there are clear advantages such as faster cooling of the cabin and better fuel economy. Furthermore, in a system based on CO_2, CO_2 can only be used as a refrigerant for refueling. This last advantage is significant since the CFCs, that deplete the ozone layer, are still being used in some countries to recharge the air conditioning units.

Tests conducted in Germany show the effectiveness of CO_2 as a refrigerant for automotive air conditioning systems. Figure 3 shows that at 28 °C, average summer temperature in Europe, the additional fuel consumption with systems that use CO_2 is significantly lower than the standard R-134a. Only under very hot conditions the additional consumption of the system that uses the CO_2 is higher than the standard, (AFA, 2009).

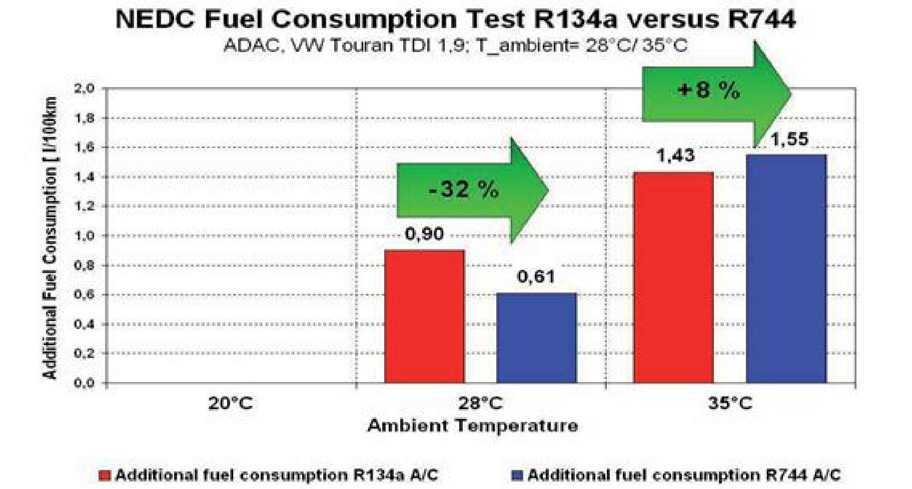

Figure 3. Fuel consumption of an R-134a MAC and an CO_2 MAC at different temperatures. AFA (2009). (ADAC)

5. THERMOPHYSICAL PROPERTIES OF HFO-1234yf AND HFO-1234ze

Critical parameters and acentric factor of HFO-1234yf and HFO-1234ze(E) are summarized in Tab. 2. Critical temperature and density were determined from the observation. Critical pressure calculated from their vapor-pressure. Acentric factor was calculated from the vapor-pressure correlations by using the critical temperature and critical pressure.

Table 2. Critical parameters and acentric factor of HFO-1234yf and HFO-1234ze(E)

	HFO-1234yf[7]	HFO-1234ze(E)[8]
Critical Temperature [K]	367.85	382.51
Critical pressure [kPa]	3382	3632
Critical density [kg/m^3]	478	486
Critical molar volume [cm^3/mol]	239	235
acentric factor	0.280	0.296

[7]: Tanaka et al. [8]: Higashi et al.

The use of modeling tools was made to calculate some of the thermophysical properties of refrigerant-HFO 1234yf as well as the performance of the theoretical system. Table 3 presents some properties of saturation and was made from the designed model with the Martin-Hou equation of state.

Table 3. Characteristic properties of Carbon Dioxide and some other traditional refrigerants

T °C	P kPa	D_{lq} kg/m^3	D_{vap} kg/m^3	H_{lq} kJ/kg	H_{latent} kJ/kg	H_{vap} kJ/kg	S_{lq} kJ/kg K	S_{vap} kJ/kg K
-40	62.197	1288.461	3.791	153.432	183.658	337.090	0.81686	1.60458
-30	98.501	1262.799	5.837	164.374	179.299	343.673	0.86268	1.60008
-20	149.908	1235.889	8.679	175.775	174.428	350.202	0.90846	1.59749
-10	220.324	1207.573	12.532	187.647	168.989	356.636	0.95423	1.59640
0	314.033	1177.653	17.648	200.000	162.925	362.925	1.00000	1.59647
10	435.640	1145.875	24.340	212.842	156.175	369.018	1.04579	1.59736
20	590.023	1111.908	32.998	226.183	148.666	374.850	1.09162	1.59875
30	782.304	1075.299	44.132	240.036	140.307	380.343	1.13749	1.60032
40	1017.859	1035.404	58.441	254.426	130.974	385.399	1.18346	1.60171
50	1302.344	991.258	76.930	269.399	120.481	389.880	1.22964	1.60248
60	1641.907	941.281	101.182	285.055	108.527	393.582	1.27628	1.60204
70	2043.480	882.550	133.992	301.615	94.541	396.156	1.32394	1.59945
80	2515.779	808.383	181.513	319.653	77.166	396.819	1.37414	1.59265
90	3072.852	693.348	266.498	341.261	51.039	392.300	1.43238	1.57292

The results presented in the table show that HFO-1234yf is very similar to HFC-134a, the refrigerant widely used in refrigeration systems with high global warming potential. Some of the data for HFO-1234yf are shown in Fig. 4 and 5 along with the same properties to HFC-134a, (Leck, 2009).

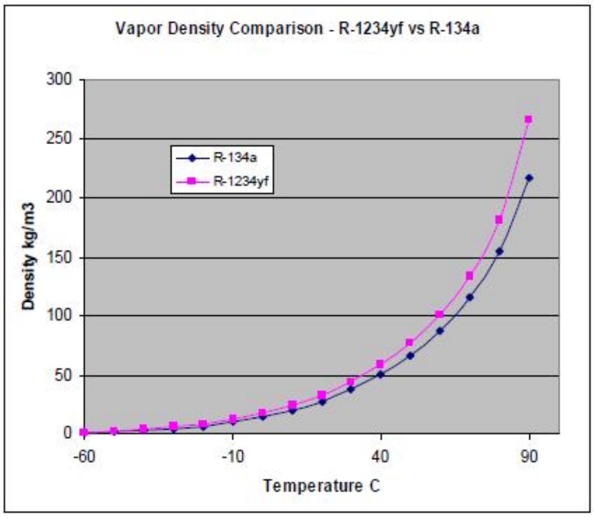

Figure 4. Vapor Density Comparison. Leck (2009).

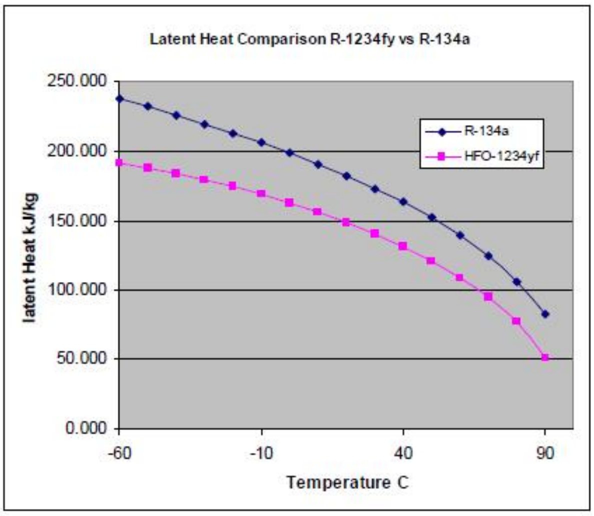

Figure 5. Latent Heat Comparison. Leck (2009).

The HFO-1234yf has low toxicity, but it is flammable and the fume produced by a fire contains hydrofluoric acid, an extremely toxic gas. Furthermore it is largely responsible for the formation of ozone in the troposphere, harmful by creating pollution in the summer and should not be confused with the useful ozone in the stratosphere.

Special attention should be given to the fact that HFC-134a, the largest source of emissions of greenhouse effect gases in the refrigeration sector, it is much cheaper than the HFO-1234yf. It is known that these products have physicochemical properties very similar, so there is a risk of fraudulent substitutions with HFC-134a during maintenance procedures. In this way, the use of HFC-134a is extended without restriction, (R744.com, 2009).

6. CONCLUSION

The prospects for the use of carbon dioxide in air conditioning systems in cars are few, at least in the short term, not because of low performance, but due to higher costs with the systems in relation to the one that use synthetic refrigerants. The biggest obstacles are its high temperature of heat rejection and system operating pressure that require proper sizing of its components.

Carbon dioxide is available in nature, is not harmful for the environment and has good thermophysical and transport properties. The challenge is to continue with researches on development, meet the market requirements in order to achieve better energy efficiency, making the system costs more compatible and making CO_2 the fluid from the future.

About HFOs only a few experimental data are available. Researches are in progress to adjust the state equations and make more reliable the data about thermophysical and transport properties. It is difficult to find a well defined opinion on its use, mainly because of their toxicity, flammability, and the formation of TFA. However it must be the transition refrigerant.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support given to the reported investigation by CAPES, CNPq and FAPEMIG.

REFERENCES

AFA, 2009. "Natural refrigerants - CO_2-based air conditioning System put to pratical testing". 26 Dez. 2010 <http:// www.umweltdaten.de/ publikationen /fpdf-l/3654.pdf>.

Antonijevic, D., 2007. "Technical and environmental aspects of synthetic refrigerants replacement by carbon dioxide in mobile air conditioning". 23 dez. 2010 <http://akson.sgh.waw.pl/ trusek/gee/papers/paper-Antonijevic.pdf>.

Antonijevic, D., 2008. "Carbon dioxide as the replacement for synthetic refrigerants um mobile air conditioning". *Journal of Thermal Science and Technology*, Vol. 12, Issue 3, pp. 44-64.

Cavallini, A., 2010. "Properties of CO2 as a refrigerant. ". 23 Dez. 2010 <http://www.centrogalileo.it/nuovapa/Articoli%20tecnici/INGLESE%20CONVEGNO/CO2/Cavallini%20-%20Milano04CO2.pdf>.

Dalang, F., 2010. "HFO-1234yf in the environment. " 26 Dez. 2010 <http://www. noe21.org /site/images/stories/Noe21/pdf/HFO-1234yf-ang.pdf>.

Higashi, Y., Tanaka, K. and Ichikawa, T., 2010. "Critical Parameters and Saturated Densities in the Critical Region for trans-1,3,3,3-Tetrafluoropropene (HFO-1234ze(E))". *Journal of Chemical & Engineering Data*, Vol. 55 (4), pp. 1594-1597.

Kim, M. H., Pettersen, J., Bullard, C., 2004. "Fundamental Process and System Design Issues in CO_2 Vapour Compression Systems", *Progress in Energy and Combustion Science*, Vol. 30, Issue 2, pp. 119-174.

Kim, M. H., Shin, J. S., Park, W. G. and Lee, S. Y., 2008. "The Test Results of Refrigerant R152a in an Automotive Air-Conditioning System", *SAE 9th Alternative Refrigerant Systems Symposium*, Scottsdale, USA.

Leck, T. J., 2009. "Evaluation of HFO-1234yf as a Potential Replacement for R-134a in Refrigeration Applications". *In 3rd IIR Conference on Thermophysical Properties and Transfer Processes of Refrigerant*, Boulder, CO, paper 155.

Nekså, P., (2002). "CO2 Heat Pumps". *Int. J of Refrigeration*, Vol. 25, Issue 4, pp 421-427.

Nekså, P., Walnum, H. T. and Hafner, A., 2010. "CO_2 - a refrigerant from the past with prospects of being one of the main refrigerants in the future. *9th IIR Gustav Lorentzen Conference 2010 - natural refrigerants - real alternatives*, Sydney, Australia.

R744.com, 2009. "New Greenpeace position paper: Four reasons against HFOs". 17 Fev. 2011 < http://www.r744.com/articles/2009-10-28-new-greenpeace-position-paper-four-reasons-against-hfos.php>.

Tanaka, K. and Higashi, Y., 2009. "Thermodynamic Properties of HFO-1234yf (2,3,3,3-tetrafluoropropene)" *In Int. J. Refrig.*, doi:10.1016/j.ijrefrig.2009.10.003.

RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.