R404A & DME ECO-REFRIGERANT BLEND AS A NEW SOLUTION TO LIMIT THE GLOBAL WARMING EFFECT

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ABSTRACT. *The paper presents the results of a theoretical thermodynamic study carried out for a single-stage vapor compression refrigeration system using a near-zeotropic refrigerant blend between R404A and Dimethylether (DME). This study is aligned to the present research strategy of finding new solutions regarding the phase out of pollutant refrigerants. By mixing R404A with DME the operating disadvantages of R404A (high saturation pressure, low mass heat load) and those of DME (high specific work input, high specific volume at the compressor inlet, flammable and explosive) are diminished. In order to establish the optimal blend DME mass fraction, a comparative thermodynamic study is carried out. REFPROP software has been used to determine the blend thermodynamic properties. The results point out the advantages of R404A substitution with the new proposed refrigerant having $(40 \div 55)\%$ DME mass fraction.*

KEYWORDS *refrigerant R404A and dimethylether blend, environment protection, vapor compression refrigeration systems, coefficient of performance, pollutant refrigerants substitution.*

1. INTRODUCTION

Romania has ratified the Vienna Convention for the Preservation of Ozone Layer, the Montreal Protocol on ozone depleting substances and its Amendments from London, Copenhagen and Montreal. The Beijing Amendment is in the approval process for incorporation into Romanian law. This emphasizes the Romanian Government's strong commitment to take the necessary measures to protect the ozone layer. Romania is classified as an Article 5 country according to the Montreal Protocol. In the period 1995 – 2001, ODS were consumed across 6 industrial sectors: refrigeration, foam, aerosol, fire fighting, solvents and fumigation.

Table 1 shows the breakdown of Romanian consumption in the different sectors in 2001 compared to 1993. The data shows that the total ODS consumption had decreased by approximately 70% by 2001 compared to 1993. The only ODS showing an increased consumption were HCFCs [1]. The refrigeration sector is the biggest remaining consumer in 2001, replacing the aerosol sector, which was the highest consuming sector in 1993 [2]. There are well known the efforts of countries to protect the ozone layer and to reduce green- house effect of the refrigerants (and avoid climate changes).

One of the result of the ozone-destroying reactions is the "ozone hole", (Fig. 1) an area of sharp decline in ozone concentrations over most of Antarctica for about two or three months during the southern hemisphere spring [2].

Table 1- Romanian ODS Consumption by sector (MT) - Comparison of 1993 with 2001 [1]

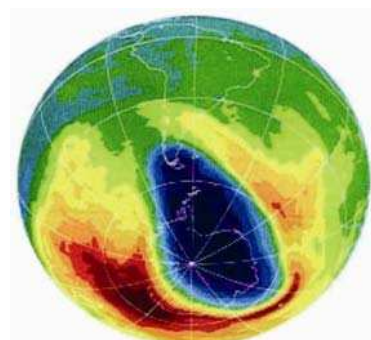| Year	Aerosol	Foam	Fire Ext.	Refrige ration	Solvent	Agricul ture	Total
1993	926	266	4	184	368	100	1849
2001	39	22	0	308	138	30	539

Fig. 1 The Antarctic "ozone hole visualization" NASA's TOMS Goddard Space Flight Centre (GSFC) [2].

In both the non-Article 5(1) and the Article 5(1) countries (see the Montreal Protocol), HCFCs and HFCs have been the primary substitutes for CFCs. In many applications, although not in all, alternatives to HCFCs have become commercially available, mainly as blends of HFCs.

As a result, HFCs have currently gained a large share of the replacement market. However, a rational approach to phase out the consumption of HCFCs, being transitional chemicals, could include a minimum time period to permit the industry to develop and commercialize alternatives. This has been applied to refrigerants but only partly to the equipment that uses the HCFCs. This approach should provide for a rational phasing in new equipment in order to avoid high costs due to the need to continue servicing existing equipment. In the short term, the transitional HCFCs are a valid, global option for refrigeration and A/C equipment [3]. However, for the long term, there remain only five important different refrigerant options for the vapour compression cycle (in addition to various non vapour compression methods):

1. hydrofluorocarbons (HFCs, HFC-blends with 400 and 500 number designation);
2. ammonia (R717);
3. hydrocarbons and blends (HCs, e.g. R290, R600, R600a etc.);
4. carbon dioxide (R744);
5. water (R718).

In this long term strategy, most of the above refrigerant options take in consideration the natural refrigerant solution [4-6]. But, none of those options are perfect; all have both advantages and disadvantages that should be considered by governments, equipment manufacturers and equipment users. For instance, HFCs have relatively high global warming potentials, ammonia is more toxic than the other options, and ammonia and hydrocarbons are flammable to certain extents. Appropriate equipment design, maintenance and use can address these concerns, though sometimes at the cost of greater capital investment or lower energy efficiency. Energy efficiency remains an important issue for all refrigeration technologies, and should be considered along with the factors enumerated above, since it is directly related to global warming. Next to ozone depletion, global warming is the main issue governing the selection of refrigerant chemicals for the near- mid- and long-term. Although this issue is not covered by the Montreal Protocol, it nevertheless forms an important criteria in the ongoing "environmental acceptability" discussion. We must take into account life cycle costs and related investment aspects. Option for energy efficient operation of equipment form is an important issue in this work. The participants, partners on this work try to solve this problem and to found ecological, natural refrigerant alternative, to phase out, CFC-chlorofluorocarbons, and HCFC- hydro chlorofluorocarbons.

2. R404A & DME COMPATIBILITY ANALYSIS

R404A (HFC 404) is a near-zeotropic refrigerant blend obtained by mixing R125/R143A/R134A pure substances in 44/52/4 mass fractions. This refrigerant has a pressure and a thermal critical point high enough (p_{cr}=37.29 bar, t_{cr}=72 °C), to be used in the best conditions as a substitute for refrigerants R502 (CFC 502) and R22 (HCFC 22) in the industrial refrigeration plants for cooling and freezing. It is not flammable and, though its ozone depletion potential is null (ODP$_{R404A}$=0), while its global warming potential is rather high (GWP$_{R404A}$=3260), R404A, together with R22, are included in the list of the pollutant refrigerants which are supposed to be prohibited on the medium term, according to the environmental protection strategies adopted worldwide [7, 8].

The dimethylether (DME), produced for the first time by Tellier in 1864, is one of the refrigerants to have been used since the beginnings of the artificial refrigeration [9], but because of its shortcomings (flammable and explosive), it has been gradually abandoned. Nowadays, on the grounds of more and more severe measures adopted for eliminating CFC, HFC and HCFC refrigerants, synthetic substances which cannot be rapidly dissociated by nature and which, being accumulated in the atmosphere become polluting refrigerants, DME becomes an interesting option. [4÷6]. DME, with a pressure and a thermal critical point (p_{cr}=53.4 bar, t_{cr}=127.15 °C) much higher than R404A, has a null ozone depletion potential and an almost null global warming potential (ODP$_{DME}$=0, GWP$_{DME}$=2).

Relying on the former refrigerant comparative studies [2], by analyzing the advantages and disadvantages of using R404A and DME respectively, one finds that, paradoxically, exactly where R404A is inadequate (high saturation pressure, low mass heat load), DME proves to be the best refrigerant among the analyzed ones. And vice versa, where DME is inadequate (high specific mechanical work input, high specific volume at the compressor inlet, flammable, explosive), R404A is great. Therefore, the main idea of this thermodynamic study becomes obvious, namely trying to reduce the disadvantages of the two refrigerants (R404A and DME) considered, by mixing them.

Eleven refrigerants are taken into consideration in the present study, mixtures of R404A and DME, for which the mass fraction in DME increases from 0%, (the mixture marked with $A0$, actually R404A) up to 100% (the mixture marked with $A10$, actually pure DME), considering a 10 % mass fraction step.
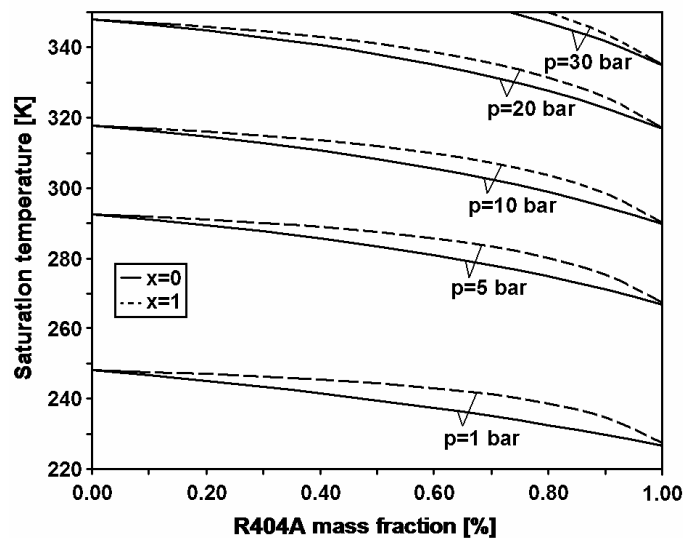

Fig. 2 Saturation temperature variation with respect to R404A mass fraction and pressure

For these blends, based on the calculations made using the **RefProp** software [10], Fig. 2 shows the variation of the saturation temperature with respect to R404A mass fraction for various pressures (p_{sat} = 1, 5, 10, 20 and 30 bar), both for the saturated liquid (x=0, marked with continuous line), as well for the dry saturated vapor (x=1, marked with discontinuous line). The figure shows that the mixtures are near-zeotropic, without zeotropic singularity point.

In order to determine which of these analyzed refrigerants is the best and which is the most recommended DME mass fraction, this paper compares the single-stage vapor compression refrigeration system performances obtained when using each of the eleven refrigerants. The performances have been determined based on the blend thermodynamic properties provided by the **RefProp** software.

3. COMPUTING METHODOLOGY

In order to prove which is the best substitute for R404A, from the eleven blend refrigerants previously defined and, respectively which is the most recommended concentration in DME, a comparative thermodynamic analysis is carried out on the theoretical performances of a single-stage compression refrigeration system (Fig. 3), operating with each of the blend refrigerants.

The theoretical analysis of the thermodynamic refrigeration cycle (Fig. 3 b), which requires a certain value of the refrigeration capacity ($\dot{Q}_0$ [kW]), has been done using the following study parameters: - evaporating temperature (t_0 [$^{\mathrm{o}}$C]); - condensing temperature (t_C [$^{\mathrm{o}}$C]); - superheating (Δt_{si} [dgr]); - subcooling (Δt_{sr} [dgr]).

Based on the values adopted for these parameters, the following have been computed:
- refrigerant temperature at the expansion valve inlet : $t_3 = t_C - \Delta t_{sr}$ [$^{\mathrm{o}}$C]　　　　(1)
- refrigerant temperature at the compressor inlet: $t_1 = t_o + \Delta t_{si}$ [$^{\mathrm{o}}$C]　　　　(2)

In order to determine the properties of the refrigerant at the compressor outlet (*2*), a compression efficiency has been estimated as ratio between saturation temperatures corresponding to compressor inlet and outlet pressure [11]:

$$\eta_c = \frac{|l_{1-2s}|}{|l_{1-2}|} = \frac{h_{2s} - h_1}{h_2 - h_1} \cong \frac{T_0}{T_c} \ [-]$$　　　　(3)
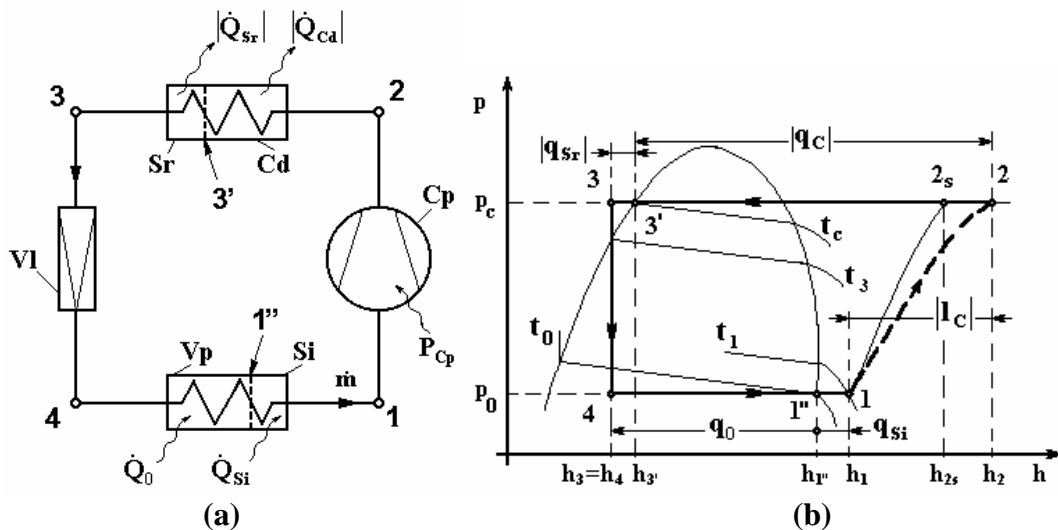

Fig. 3 Configuration (a) and thermodynamic cycle (b) of the refrigeration system

Moreover, the specific mass and volume cooling loads have been computed with:
- the evaporator mass cooling load: - the evaporator volume cooling load:

$$q_0 = q_{4-1"} = h_{1"} - h_4 \ [\text{kJ/kg}] \qquad (4); \qquad q_{Vo} = q_0/v_1 \ [\text{kJ/kg}] \qquad (5)$$

where $v_1 \ [\text{m}^3/\text{kg}]$ represents the refrigerant specific mass volume at the compressor inlet.
- the specific mass mechanical work input: - the condenser specific mass heat load:

$$|l| = |l_{1-2}| = h_2 - h_1 \ [\text{kJ/kg}] \qquad (6); \qquad |q_C| = |q_{2-3`}| = h_2 - h_{3`} \ [\text{kJ/kg}] \qquad (7)$$

- the overheating specific mass heat load: - the subcooling specific mass heat load:

$$q_{si} = q_{1"-1} = h_1 - h_{1"} \ [\text{kJ/kg}] \qquad (8); \qquad |q_{sr}| = |q_{3`-3}| = h_{3`} - h_3 \ [\text{kJ/kg}] \qquad (9)$$

- verifying the energy balances: - the coefficient of cooling performance:

$$q_0 + q_{si} - |q_C| - |q_{sr}| = -|l| \qquad (10); \qquad COP = \frac{q_o}{|l|} \ [\text{-}] \qquad (11)$$

And the refrigerant mass and volume flow rates at the compressor inlet have been computed with:
- the refrigerant mass flow rate: - the compressor inlet volume flow rates:

$$\dot{m} = \dot{Q}_o/q_o \ [\text{kg/s}] \qquad (12); \qquad \dot{V}_a = \dot{m} \cdot v_1 \ [\text{m}^3/\text{s}] \qquad (13)$$

4. RESULTS

Using the computing methodology described before, for a refrigeration capacity of $\dot{Q}_0 = 30$ kW and for the following values of the analyzed parameters $t_C = +40^{\circ}\text{C}$; $\Delta t_{sr} = 10 \text{ dgr}$; $\Delta t_{si} = 20 \text{ dgr}$, calculations have been made for various vaporization temperatures $t_0 = -25^{\circ}\text{C} \div +10^{\circ}\text{C}$, with 5dgr as step.

The values of the thermodynamic proprieties (p pressure, t temperature, h enthalpy, s entropy and v specific volume) in the characteristic points of the theoretical cycle [8] (thermodynamic states $1"-1-2s-2-3`-3-4$) have been determined by using programs developed in *RefProp* software, for each of the considered refrigerants (from the $A0$ blend, with DME 0%, up to $A10$ blend, with DME 100%, with 10% as step).
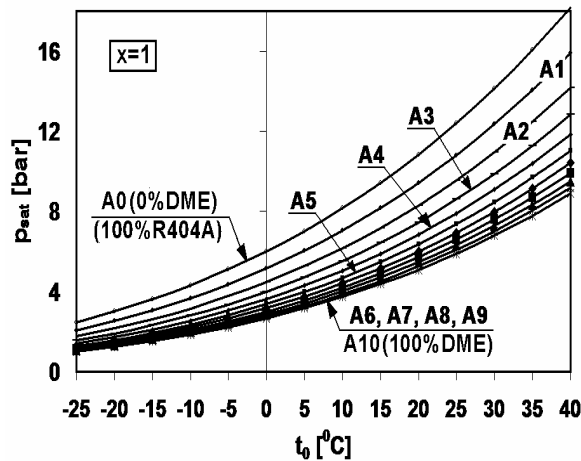

Fig. 4 Saturation pressure variation with respect to evaporate temperature for dry saturated vapor (x=1)
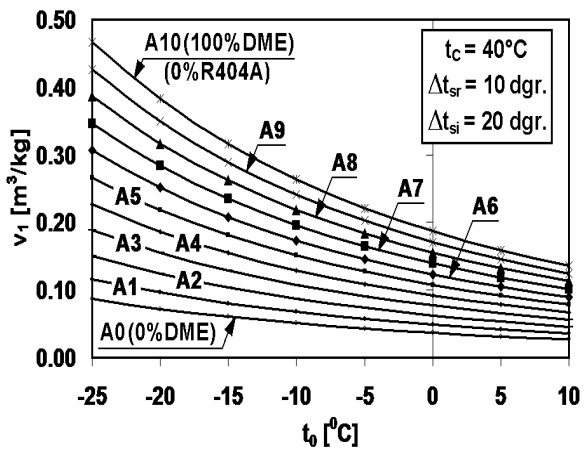
Fig. 5 Specific mass volume at the compressor inlet variation with respect to evaporating temperature

Thus, Fig. 4 shows the variation of the saturation pressure $p_{sat}(t)$ with respect to evaporating temperature (t_0) for each of the studied blend refrigerants. One may notice that the saturation pressure decreases significantly up to a 50% mass fraction in DME. The

decrease of the saturation pressure with the increase of the DME mass fraction is an important advantage in case of blending R404A with DME. When the mass fraction of DME increases above 50% the decrease of the saturation pressure is smaller and smaller.

Fig. 6 presents the variation of refrigerant specific mass volume at the compressor inlet (v_1) with respect to evaporating temperature (t_0) for each of the studied blend refrigerants. At $t_0 = ct.$, it results a monotone increasing of v_1 with DME mass fraction increase.

The variation of the refrigeration system COP with respect to DME mass fraction shown in Fig. 6 points out the following important aspects:

- for low evaporating temperatures (-25°C ÷ -20°C), the COP increases continuously with the increase of DME mass fraction. This fact recommends the use of a refrigerant with a high DME mass fraction, but at the same time the flammability and the explosive potential of the mixture increase;

- for medium and high evaporating temperatures (-15°C ÷ +10°C), the COP presents a minimum value corresponding to a certain DME mass fraction between 20% and 40%, which should be avoided.

In order to underline the advantage obtained by replacing R404A with one of the mixtures $Ax \in (A0 \div A10)$ for a given evaporating temperature, the term of relative COP increase is defined:

$$\overline{\Delta COP} = \frac{COP(Ax) - COP(A0)}{COP(A0)} 100 \quad [\%] \tag{14}$$
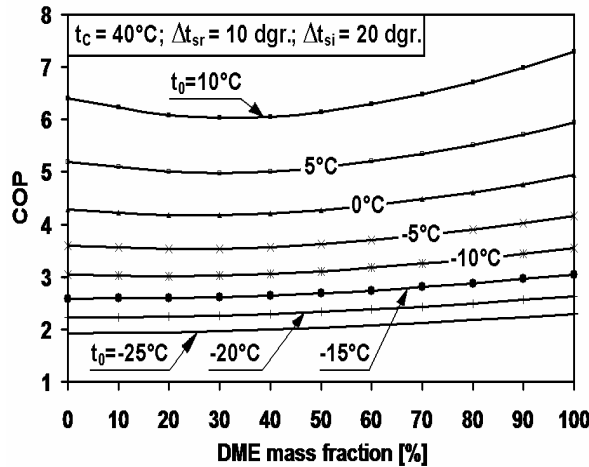

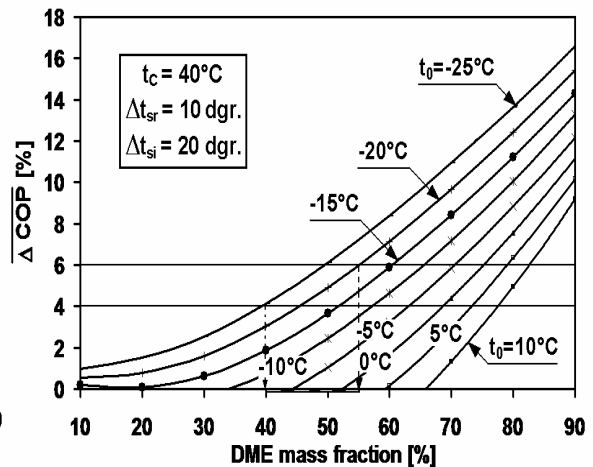Fig. 6 COP variation with respect to DME mass fraction for different evaporating temperatures

Fig. 7 Relative COP increase variation with respect to DME mass fraction and evaporating temperature

Therefore, based on the relation (12), Fig. 7 presents the relative COP increase with respect to R404A operation case and DME mass fraction, for different evaporating temperature ranges taken into consideration. In conclusion, by replacing R404A with a more ecological refrigerant obtained through blending R404A with DME, the increase of the COP may have values from (1 ÷ 16)%, for low temperature applications (LT), values from (1 ÷ 12)%, for medium temperature applications (MT) and, respectively values from (1 ÷ 9)%, for air conditioning (AC).

For instance, if one wants a relative COP increase by (4 ÷ 6)%, then, as shown in Fig. 5, depending on the thermal conditions in the evaporator, the following mass fraction values need to be adopted :

- for LT: (40 ÷ 55)% in DME;   - for MT: (52 ÷ 70)% in DME;   - for AC: (68 ÷ 83)% in DME.

5. CONCLUSIONS

The paper presents the results of the thermodynamic theoretical analysis on the possibility of replacing the polluting CFC, HFC and HCFC refrigerants, especially R404A, with more ecological refrigerants obtained by blending R404A with dimethylether. The thermodynamic analysis is carried out for a single-stage vapor compression refrigeration system using as a refrigerant near-zeotropic blends, without zeotropic singularity point, obtained by mixing, in various proportions R404A with dimethylether (DME). Thus, eleven types of refrigerant mixtures are taken into consideration, and for each of them the mass fraction of DME increases from 0% (the mixture marked with $A0$) up to 100% (the mixture marked with $A10$), with a step of 10%.

By comparing the results for the thermodynamic performances of the refrigeration system functioning in the same required conditions (refrigeration capacity, evaporating and condensing temperatures) with R404A and, respectively, with studied refrigerant blends, the following advantages resulted:
- operation at a lower pressure level, without any vacuum risk;
- higher evaporator mass heat load, thus, lower refrigerant mass flow rate;
- lower power consumption;
- higher COP.

Also, the thermodynamic results obtained underline the fact that blending R404A with DME has as main disadvantage the need to use compressors with bigger displacement and dimensions.

In case of replacing R404A with a mixture of R404A and DME, if one wants the COP increased by $(4 \div 6)\%$, based on the calculations performed, it has been shown that, depending on the thermal conditions of the evaporator, the mass fraction of DME must be, as follows: for LT applications $(40 \div 55)\%$, for MT applications $(52 \div 70)\%$ and $(68 \div 83)\%$ for AC applications.

As a result, the theoretical research done in this paper points out important advantages given by replacing R404A with a R404A and DME mixture, which fully justifies the new solution proposed for the replacement of the polluting refrigerants. Taking into consideration that, together with the increase of DME mass fraction , there is also an increase of the flammability and explosive indexes of the mixture, this study demonstrates that the new group of suggested refrigerants is recommended especially for LT applications, in which case the recommended DME mass fraction is between $(40 \div 55)\%$.

In order to actually prove that the mixture of R404A with DME is a viable practical solution for the replacement of the polluting refrigerants, there is the need to carry out experimental research for confirming the endurance and reliability performances.

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