THERMODYNAMIC ANALYSIS OF NEW ECO-
REFRIGERANTS AMMONIA AND DIMETHYLETHER
BLENDS

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Rezumat. Lucrarea prezintă o parte din rezultatele studiului termodynamic teoretic al unei instalaţii frigorifice cu o treaptă de comprimare de vapoare (IFV). Sistemul frigorific foloseşte ca agent de lucru amestecuri obţinute dintre amoniac (R717) şi dimetileter (DME). Acest nou tip de agent frigorific este în general un amestec neazeotrop, dar pentru o presiune dată prezintă punct singular de azeotrop. La acelaşi impact ecologic ca şi amoniacul (ODP=0, GWP≈0), unele din aceste amestecuri au proprietăţi termodynamicale mai bune. Să fim bine să vă amintim faptul că această soluţie lui R7171 cu noii agenţi frigorifii de tip amestec R717 şi DME, care permit extinderea domeniului de aplicaţie şi pentru instalăriile de condionare a aerului.

Cuvinte-cheie: substituţia agenţilor frigorifici neecologici; amestecuri între R717 şi DME; instalaţii frigorifice cu comprimare de vapor; coeficient de performanţă.

Abstract: The paper presents the results of a theoretical thermodynamic study carried out for a single-stage vapor compression refrigeration system (IFV). The refrigeration system uses as working fluids mixtures obtained by blending ammonia (R717) and dimethylether (DME). These new refrigerants are generally zeotropic blends, but for a given pressure they have an azeotropic behaviour. At the same ecologic characteristics as ammonia (ODP=0, GWP≈0), some of these new mixtures have better thermodynamic properties than those of pure ammonia. RefProp software has been used to determine the blends thermodynamic properties. At optimal blend DME mass fractions (35 ÷ 45)%, corresponding to azeotropic states, the results point out the advantages given by replacing R717 with the new eco-refrigerants, which allows to extend the field of application from air conditioning to refrigeration.

Keywords: substitution of non-ecological refrigerants/R717 & DME blends/vapor compression refrigeration systems/coeficient of performance.

1. INTRODUCTION

Due to its excellent thermodynamic properties, ammonia (R717) is one of the oldest and best refrigerants. It has high pressure and critical temperature ($p_{cr} = 113.33$ bar, $t_{cr} = 132.25$ °C) and the highest latent heat of vaporization among known refrigerants (1370.25 kJ/kg, at 1 bar). Ammonia has been (Kuprianoff et al. 1956) and it is still (Marinescu et al. 2004) successfully used in vapor compression refrigeration systems (IFV). It is a natural refrigerant having ODP$_{R717}=0$ and GWP$_{R717}=0$. Because of its drawbacks like, risk of explosion (minimum 15% vol.), flammability (-2°C), destructive action over some commonly used materials in refrigeration systems (copper, aluminum and rubber), toxicity and strong odor, the use of ammonia has significantly decreased since 1930 when began the production of synthetic refrigerants (CFC’s, HCFC’s and HFC’s), which are neither toxic nor flammable.

Currently, due to the environmental issues regarding ozone layer depletion and accentuation of the greenhouse effect, partially generated by the intensive, extensive and long term use of CFC’s, HCFC’s and HFC’s, the tendency of using ammonia has inverted (Marinescu et al. 2004, Târlea et al. 2006). Development of the helical

compressor determined increasing use of R717 in vapor compression refrigeration systems, because it solved the problems related to discharge temperature that occur in case of using reciprocating ammonia compressors.

Presently, for modern ammonia refrigeration systems there is a tendency of minimizing the refrigerant charge, leading to increased security. Refrigerant charge can be reduced by using intermediary fluids, cold carriers, and indirect expansion systems.

This paper presents another method to reduce the refrigerant charge and to increase security by replacing R717 with a blend of R717 and dimethylether (DME).

DME (RE170) is a chemical substance obtained through methanol synthesis. This substance was used for the first time as a refrigerant by Tellier in 1864. So, DME is one of the first refrigerants ever used for artificial refrigeration (Kuprianoff et al. 1956). It was gradually abandoned as a result of its drawbacks generated mainly by the explosion risk (minimum 3.4% vol.) and flammability (-41°C).

Currently, based on the increasingly harsh actions taken in order to eliminate the CFC’s and HCFC’s, synthesis compounds that have long atmospheric life, DME becomes a refrigerant of interest (Marinescu et al. 2004, Târlea et al. 2006, Lorentzen and Pettersen 1992, Lorentzen 1993 and 1995). DME, has lower pressure and critical temperature ($p_{cr}=53.4$ bar, $t_{cr}=127.15$ °C),
lower latent heat of vaporization (461.91 kJ/kg, at 1 bar) than R717, ODP_{DME}=0 and GWP_{DME}=2.

As a result of previously comparative studies (Marinescu et al. 2004), analyzing the advantages and disadvantages of using R717 in vapor compression refrigeration systems and DME, respectively, as well as their reciprocal compatibility, it emerges the idea which is the ground of this thermodynamic study, namely to reduce the disadvantages of R717 (relatively high saturation pressure, high mass specific mechanical work, high compressor discharge temperature, toxicity) and those of DME (high specific mass volume at the compressor inlet) through their reciprocal combination. Besides obtaining new competitive eco-refrigerants, this idea allows to extend the use of R717/DME blend from air conditioning (AC) to refrigeration applications and reduction of R717 mass charge.

As support for the new proposed eco-refrigerants, there is a mixture between R717 and DME – (60/40)% mass fraction - which has been used as a refrigerant by the Austrian company FRIGOPOL since 2003 (Herunter 2003). This refrigerant with the molecular mass of 22.772 kg/kmol, although it is not 100% natural, was designated by the manufacturer with the indicative R723. Comparing with pure R717, for R723 the solubility for mineral oil and specific heat capacity is considerably improved (Krauss and Schenk 2007).

In the present thermodynamic study, eleven refrigerants, R717/DME blends have been taken into consideration, for which the DME mass fraction increases from 0%, (the blend referred to as A0, i.e. pure R717) to 100% (the blend referred to A10, i.e. pure DME), with a mass fraction step of 10%. Consequently, R723 is noted with the indicative A4.

For these blends (calculations made using the RefProp software - Lemmon 2007), figures 1 and 2 show the variation of the saturation temperature and the latent heat of vaporization with respect to R717 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).

Figure 1 shows that the obtained blends are zeotropic, with an azeotropic state at a given pressure. The locus of azeotropic states is represented with a dotted line. Figure 2 shows the significant drop of the latent heat of vaporization with the increase of DME mass fraction. Consequently, R723 has approximately 30% lower latent heat of vaporization than pure R717.

From figure 1 one can notice the fact that the blends with a DME mass fraction within (35 ÷ 45)%, including R723, are near-azeotropic at low saturation pressures (1 ÷ 5 bar) and azeotropic, respectively, at higher saturation pressures than 5 bar. This represents very important advantage for the industrial use of the new refrigerants, since they do not cause any problems neither in maintaining their initial composition during the charging process, nor in case of gas leaks on the high pressure side.

In order to establish which of the suggested new refrigerants is most recommended and which is the most appropriate DME mass fraction, this study compares the performances obtained when using all of these eleven refrigerants in a single-stage vapor compression refrigeration system working in the same conditions. The calculation of these performances was carried out based on their thermodynamic properties given by RefProp software.

![Figure 1. Saturation temperature depending on the pressure and R717 mass fraction.](image1)

![Figure 2. Latent heat of vaporization depending on the pressure and R717 mass fraction.](image2)

### 2. CALCULATION METHODOLOGY

In order to point out the optimum DME mass fraction and which of the eleven analyzed refrigerants is best suited for substituting R717, a comparative thermodynamic analysis was carried out, regarding the theoretical performances of a single-stage vapor compression refrigeration system (IFV). The constructive scheme and thermodynamic theoretical cycle in p–h diagram, for a zeotropic refrigerant blend between R717 and DME, are presented in figures 3 a and b.

The thermal calculation of the thermodynamic refrigeration cycle (figure 3 b) asserting the same cooling load (\( Q_c \) [kW]), for all types of analyzed refrigerant blends, based on R717 and DME, has been performed by applying the following study parameters:

- evaporation temperature (\( t_0 \) [°C]);
- condensing temperature (\( t_c \) [°C]);
- overheating degree (\( \Delta t_h \) [deg.]);
- subcooling degree (\( \Delta t_{sr} \) [deg.]);

Based on the values adopted for these parameters the following have been calculated:

\[
 t_3 = t_c - \Delta t_{sr} \ [°C] \tag{1}
\]
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– refrigerant temperature at the compressor inlet:
\[ t_1 = t_0 + \Delta t_u \ [^\circ C] \quad (2) \]

After checking the cycle energy balance, for 1 kg of refrigerant:
\[ q_o + q_w - q_h - q_v = -\Delta t \]
the coefficient of performance is:
\[ COP = \frac{q_o}{\Delta t} \quad [-] \quad (10) \]

In order to assess the values of the actual discharge parameters, state (2), the value of compression efficiency, as ratio of the absolute saturation temperatures, corresponding to discharging and suction pressures has been approximated (Popescu et al. 2005):
\[ \eta_c = \frac{T_o - T_s}{T_o - T_i} \approx \frac{T_o}{T_c} \quad [-] \quad (3) \]

The specific exchanged energy on the theoretical thermodynamic cycle of IFV has been calculated as follows:

– evaporator mass heat load:
\[ q_o = q_{p-1} = h_e - h_l \ [\text{kJ/kg}] \quad (4) \]

– evaporator volume heat load:
\[ q_{v1} = q_o / v_1 \ [\text{kJ/kg}] \quad (5) \]

where \( v_1 \ [\text{m}^3/\text{kg}] \) is the specific volume of the refrigerant at the compressor inlet.

– compressor specific mechanical work input:
\[ |\| = |h_i - h_o| = h_s - h_l \ [\text{kJ/kg}] \quad (6) \]

– condenser mass heat load:
\[ q_c = |h_2 - h_3| = h_2 - h_3 \ [\text{kJ/kg}] \quad (7) \]

– overheating mass heat load:
\[ q_{hi} = q_{v-1} = h_l - h_v \ [\text{kJ/kg}] \quad (8) \]

– subcooling mass heat load:
\[ q_{si} = |h_3 - h_4| = h_3 - h_4 \ [\text{kJ/kg}] \quad (9) \]

The mass and volume flow rates at the compressor inlet, have been calculated:
\[ m = \frac{q_o}{\Delta t_o} \ [\text{kg/s}] \quad (11) \]
\[ V_{p1} = m \cdot v_1 \ [\text{m}^3/\text{s}] \quad (12) \]

3. RESULTS

Using the previously shown calculation methodology (chapter 2), for a cooling load of \( Q_o = 30 \text{ kW} \) and for the following values of the study parameters \( t_c = +40 \ ^\circ C \); \( \Delta t_w = 10 \ ^\circ C \); \( \Delta t_s = 20 \ ^\circ C \), calculations were made for different evaporation temperatures \( t_o = -25 \ ^\circ C \div +10 \ ^\circ C \), asserting a step of 5 \(^\circ C\). The range chosen for evaporation temperature refers to low temperature, refrigeration and AC applications.

State parameters (pressure \( p \), temperature \( t \), enthalpy \( h \), entropy \( s \) and specific volume \( v \)) in the specific points of the theoretical thermodynamic cycle of IFV (1’–1–2s–2′–3–3′–4), in figure 3 b, have been determined by using calculation programs developed in RefProp software, for each of the eleven considered refrigerants (from \( A_0 \) blend, containing 0% DME, up to the \( A_{10} \) blend, containing 100% DME, at an interval of 10%); the R723 refrigerant being referred to as \( A_{4} \).

Thus, in figure 4 the variation of the evaporator mass heat load (\( q_o \)) is presented as depending on the evaporation temperature (\( t_o \)) for each of the eleven types of refrigerants. It results, that for a certain type of blend (\( A_0 \div A_{10} \)), \( q_o \) practically does not depend on \( t_o \). In turn, \( q_o \) decreases upon the increase of DME mass fraction. Thus, for R723 refrigerant (\( A_{4} \) blend) \( q_o \) decreases by more than 30% in comparison with pure R717 refrigerant (\( A_{0} \)).

Fig. 3. Scheme (a) and theoretical thermodynamic cycle in \( p - h \) diagram for a zeotropic refrigerant blend between R717 and DME (b) of IFV.

Fig. 4. Variation of the evaporator mass heat load depending on the evaporation temperature.
In all diagrams, as indicated in figure 5, the situations in which the compressor discharge temperature exceeds the maximum allowed value $t_2^\text{max} = 140 \, ^\circ\text{C}$ (to avoid oil deterioration) have been represented by a dotted line.

Figure 5 shows that, under imposed conditions the refrigeration systems taken into consideration may work based on pure R717 only for AC applications ($t_0 \geq 0 \, ^\circ\text{C}$).

Fig. 5. Variation of $t_2$ depending on $t_0$ and the DME mass fraction

Under these circumstances, figure 5 highlights the advantage of reducing the discharge temperature by increasing the DME mass fraction, in case of replacing R717 with R717/DME blends. Thus, it results that the R723 refrigerant may also be used in good conditions in refrigeration application area (-15°C < $t_0$ < 0°C).

Figure 6 highlights the disadvantage that the saturation pressure increases with the increase of DME mass fraction, for the (0 ÷ 55)% range. This increase is of maximum 16% for temperatures corresponding to AC applications, while for low temperature applications it becomes much higher (maximum 20%).

Therefore, at a certain constant evaporation temperature, the saturation pressure of R717/DME blends is lower than that of pure R717 only for high DME mass fraction (approximately over 80%).

Fig. 6. Variation of the saturation pressure depending on $t_0$ and DME mass fraction.

The COP variation, depending on the evaporation temperature and DME mass fraction, is shown in figure 7. It results that, for the same evaporation temperature, the increase of DME mass fraction, within (0 ÷ 55)% range, including R723, determines a COP equal to the one of pure R717 ($A_0$). The COP is lower for almost all other blends.

Fig. 7. Variation of COP depending on $t_0$ and DME mass fraction.

Figure 8 displays the variation of the evaporator volume heat load for R717/DME blend depending on the evaporation temperature and DME mass fraction. It results that, for a certain evaporation temperature, within (0 ÷ 55)% range the evaporator volume heat load increases with the increase of DME mass fraction. This represents a very important advantage obtained when substituting R717 with a blend having a DME mass fraction especially within (35 ÷ 55)% range.

Fig. 8. Variation of the evaporator volume heat load depending on $t_0$ and DME mass fraction.

The variation of refrigerant volume flow rate at the compressor inlet depending on the evaporation temperature and DME mass fraction under imposed conditions and a cooling load of $Q_c = 30 \, \text{kW}$, is shown in figure 9.

Fig. 9. Variation of $\dot{V}_c$ depending on $t_0$ and DME mass fraction.

It results that with the increase of DME mass fraction within (0 ÷ 55) % range, the refrigerant volume flow rate at the compressor inlet has the same values.
when using pure R717 \((A0)\) for \(AC\) \(t_0 \in (0 \pm 10)\)°C, as well as for refrigeration applications \(t_0 \in (0 \pm 10)\)°C.

This represents another important advantage in case of replacing R717, in an existing IFV, with the new proposed near-azeotropic blend containing \((35 \pm 45)\)% DME mass fraction, which allows the use of the same compressor.

4. CONCLUSIONS

This paper presents the results of a theoretical thermodynamic analysis over the possibilities of the ammonia (R717) use, as natural ecologic refrigerant, in vapor compression refrigeration systems (IFV), for the substitution of non-ecological refrigerants (CFC’s, HCFC’s and HFC’s).

Thus, in order to obtain the extension of R717 application in AC and refrigeration area and to reduce the R717 mass load, this paper analyzes the possibility of substituting R717 with a new family of working fluids obtained by blending R717 and dimethylether (DME).

As R717 (natural substance) and DME (non toxic synthetic substance) are environmentally-friendly, the blends between them are eco-refrigerants \((ODP=0, GWP \approx 0)\), less toxic than R717 in pure state. Mixing R717 and DME has as result zeotropic mixtures with an azeotropic state at a given pressure. At an optimal range of DME mass fraction, the majority of its thermophysical properties are better than those of pure R717. As support for this study the R723 agent is known, a blend of R717/DME with \((60/40)\)% mass fractions used by FRIGOPOL company from Austria. Comparing with pure R717, for R723 the solubility for mineral oil and specific heat capacity is considerably improved.

In order to determine the optimal DME mass fraction of the zeotropic blends proposed here as new eco-refrigerant, a one-stage vapor compression refrigeration system (IFV) has been thermodynamically investigated. Therefore, eleven types of refrigerant blends were considered, with DME mass fraction increasing from 0\% (pure R717, blend referred to as A0) to 100\% (pure DME, blend referred to as A10) with 10\% step.

After having compared the thermodynamic performances of the considered refrigeration system operating in the same imposed conditions (cooling load, evaporation and condensing temperatures, overheating and subcooling degrees) based on R717 and on blends with \((35 \pm 45)\)% DME mass fraction, the following advantages emerged:

- being azeotropic blends at higher pressures than 5 bar, they do not cause any problems neither in maintaining their initial composition during the charging process, nor in case of gas leaks on the high pressure side;
- higher volume heat load \((2\% \pm 5\%)\), for the same volume flow rate at the compressor inlet;
- lower compressor discharge temperature \((25^\circ C \pm 35^\circ C)\) which allows to extend the use of R717/DME blend from AC to refrigeration applications.

The thermodynamic results also highlight the fact that the main disadvantage of mixing R717 with DME is the reduction of the evaporator mass heat load, but without lowering the COP. The increase of the operating pressure with maximum 20\% is another disadvantage, but without increasing the power consumption more than 3\%.

Consequently, the theoretical results highlight important advantages of replacing R717 with a R717 and DME blend, which fully justifies the new proposed family of refrigerants. Taking into account the fact that once DME mass fraction increases, flammability and explosiveness indexes also increase, the newly suggested refrigerants are especially recommended for AC and refrigeration applications, where DME mass fraction should be within the range of \((35 \pm 45)\)%. This recommendation, as a result of the thermodynamic analysis, confirms that R723 refrigerant, with 40\% DME mass fraction, which has been already used in practice, guarantees the advantageous substitution of pure R717.

In order to effectively demonstrate that R717 and DME blends represent a reliable and practical solution in replacing the non-ecological refrigerants, in general, and R717 in particular, experimental investigations to confirm performances, endurance and reliability are needed.

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