

## SINGLE STAGE ABSORPTION SYSTEM BASED ON REFRIGERANTS R125 AND R134A WITH DMETEG.

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### ABSTRACT

Current developments in absorption technology include the research for new working pairs and new advance cycles that would facilitate increased efficiency of absorption units and extend applicability to different temperature ranges. Two refrigerants tetrafluoroethane (R134a) and pentafluoroethane (R125) that are alternatives to chlorofluorocarbons, in combination with absorbent dimethylether teraethylene glycol (DMETEG) were evaluated for possible utilization in absorption machines powered by low temperature heat sources.

A computerized simulation program was used to compare the different refrigerant-absorbent pairs. The program was based on an advance single-stage cycle containing a jet ejector. The absorption cycle was represented in terms of heat and mass balance for each component and the calculations were based on the thermophysical properties of the refrigerant-absorbent pairs measured and evaluated in our laboratory. The aim of the cycle analysis was to evaluate the highest coefficient of performance (COP) and the lowest circulation ratio ( $f$ ), which can be obtained for different generator temperatures under a constant evaporating and cooling water temperatures. The effects of changes in the evaporator and the cooling water temperatures on the COP and the circulation ratio,  $f$ , were also examined at the generator temperature at maximum COP.

### INTRODUCTION

Utilization of available heat sources for cooling and refrigeration can be implemented by various types of absorption heat pumps, both single and multi-stage. However, the utilization of low potential heat sources for cooling and refrigeration ( $<0^{\circ}\text{C}$ ) is limited by the properties of the working fluids and the cycle configuration of the heat pump. For utilization of low potential heat sources ( $80\text{--}140^{\circ}\text{C}$ ) for cooling and refrigeration to below  $0^{\circ}\text{C}$ , a single-stage absorption heat pump based on organic working fluids is preferable, since conventional working fluids such as ammonia-water or water-lithium bromide are limited to the above described operation conditions.

The temperature of the heat source and the cooling or refrigeration demands are usually the factors that determine the type of working fluid to be used and the type of the absorption heat pump system required—single or multistage.

The commonly used working fluids are ammonia-water or water-lithium bromide. The ammonia-water combination

requires a heat source temperature above  $120^{\circ}\text{C}$  for cooling and refrigeration to  $<0^{\circ}\text{C}$ . Such a system is a high-pressure system that requires a rectification column (Engler et al., 1997). Ammonia has acceptable thermophysical properties, but it is a flammable fluid that is toxic and strongly irritant and is corrosive to copper.

The water-lithium bromide solution can be used with a heat source temperature above  $70^{\circ}\text{C}$  for air-conditioning but not for cooling and refrigeration because of the limitation for the evaporator temperature ( $>0^{\circ}\text{C}$ ). This system operates under vacuum. The water-lithium bromide solution is highly corrosive and extremely viscous and viscosity-reducing agents are frequently required. The limitations of using common working fluids (Thioye, 1997) for utilizing of low potential heat sources ( $80\text{--}120^{\circ}\text{C}$ ) for cooling and refrigeration ( $<0^{\circ}\text{C}$ ) are thus self-evident.

To overcome these limitations, working fluids based on fluorocarbon (HFC) refrigerants and organic absorbents have been chosen (Borde et al., 1995, 1997, Jelinek & Borde, 1999 and Sawada et al., 1994). The refrigerants are not toxic or corrosive and the organic working fluids are environmentally acceptable. In these high-pressure systems, the condenser and the absorber are water cooled, and a rectification column is not needed, since the difference between the normal boiling points of the absorbent and the refrigerant is about  $200^{\circ}\text{C}$ .

In order to evaluate the performance of the candidate refrigerant-absorbent pairs in a refrigeration or heat pump cycle in terms of the coefficient of performance (COP) and the circulation ratio ( $f$ ), the thermophysical properties of the pure components and the mixtures at equilibrium have to be determined from experimental or published data or by prediction methods. Then, the COP and  $f$  can be calculated with the aid of a computerized simulation program based on a single-stage absorption cycle containing a jet ejector mixer (Daltrophe et al., 1993) with a refrigerant heat exchanger HR.

The results of the investigation are presented as a model working fluid, and a comparison of R125-DMETEG with other refrigerant and the same absorbent, i.e., R134a-DMETEG, was made.

### THERMODYNAMICS DIAGRAMS

With the aim of screening of large numbers of potentially interesting working fluids for absorption cycles, we designed and built an experimental setup and developed an evaluation

methodology that permits measurement of large amounts of data with sufficient accuracy for generation of equilibrium properties of refrigerant-absorbent pairs (Borde et al., 1995, 1997, Jelinek & Borde, 1999).

The temperature up to 150°C and the pressure in the vessel up to 20 bars were measured at equilibrium. For each set of measurements, the reactor was weighed so that the total weight of the refrigerant and the absorbent in the vessel were known. The temperature was increased, and at equilibrium the pressure was measured. At the end of each set of measurements, the vessel was cooled down to the ambient temperature, a certain amount of gas was released, and the reactor was weighed again. From the amount of gas released, the amount of absorbent vapor released was estimated. This procedure was repeated up to the end of the experiment. The method of calculation of the concentration in the liquid and gas phases as a function of temperature and weight fraction based on our experimental setup is given by Jelinek & Borde (1999).

Based on the above-mentioned measurements, a polynomial relationship linking the concentration, temperature and pressure,  $p(T, \xi)$ , under equilibrium conditions was obtained. The polynomial coefficients were obtained by regression of all the points determined by the equilibrium measurements and the additional pure component vapor pressure, using the Statistical Package for Social Sciences (SPSS).

#### Thermodynamic Data of the Pure Components

The basic data for the pure components, i.e., molecular weight, normal boiling point, critical temperature and critical pressure, are given in Table 1.

Table 1: Thermodynamic data for the pure components

	formula	$M_w$	$T_b$ [°C]	$T_c$ [°C]	$p_c$ [bar]
R134a	$\text{CH}_2\text{FCF}_3$	102.03	-26.5	101.1	40.67
R125	$\text{CHF}_2\text{CF}_3$	120.02	-48.5	66.2	39.29
DMETEG	$\text{C}_{10}\text{H}_{22}\text{O}_5$	222.29	275.3	440.2	19.53

#### Excess Thermodynamic Properties

The excess molar Gibbs energy of mixing  $G^E$  is the point of departure for calculating other excess properties.  $G^E$  of a solution expressed in terms of the molar weight fraction and the activity coefficient is given as;  $G^E = RT \sum (x_i \ln \gamma_i)$ . The UNIFAC model (Fredenslund et al., 1977) was used to evaluate the activity coefficient  $\gamma$  in the liquid phase and for calculation of the molar excess enthalpy  $H^E$  of the mixture. The specific excess enthalpy  $h^E$  of the mixture is expressed as a polynomial relationship linking the concentration, temperature with the excess enthalpy  $h^E(T, x)$ , where  $h^E$  is given in kJ/kg and  $x$  is the mole fraction of the refrigerant in the liquid solution. The polynomial coefficients were obtained by regression of all the points calculated by the UNIFAC model, using the SPSS. It should be noted that the UNIFAC model was used solely in order to evaluate the excess properties required for constructing enthalpy-concentration diagrams. The specific excess enthalpy,  $h^E$ , as a function of the temperature and the molar fraction was then used to calculate the enthalpy concentration diagram.

#### Enthalpy-Concentration Diagrams

From the specific enthalpy of the pure components and the specific excess enthalpy of mixing, the enthalpy of the solution in the liquid phase, which consists of the sum of the weighted

contributions of the two components, can be calculated as follows;

$$h = h_r \xi + (1 - \xi) h_a + h^E \quad (1)$$

The enthalpy-concentration diagrams for R125-DMETEG and for R134a-DMETEG as a function of the weight fraction of the refrigerant for a set of isobars and isotherms at equilibrium are presented in figures 1 and 2, respectively.

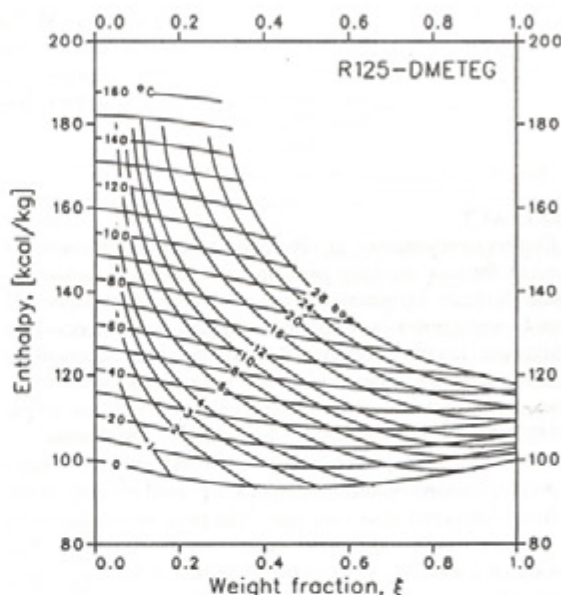


Figure 1: Enthalpy-concentration diagram for R125-DMETEG

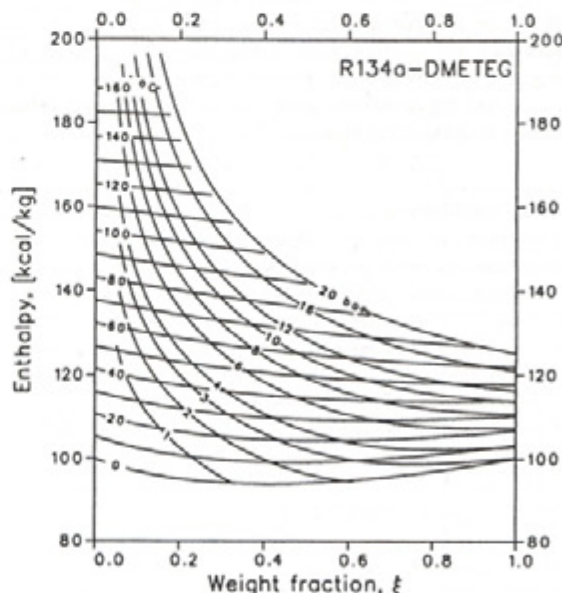


Figure 2: Enthalpy-concentration diagram for R134a-DMETEG

### SINGLE-STAGE ABSORPTION CYCLE

The performance characteristics of the investigated working fluids in terms of COP and  $f$  were based on the thermodynamic calculation of a single-stage absorption cycle containing a jet ejector mixer with a refrigerant heat exchanger HR. The cycles are presented schematically in figure 3.

#### Theoretical Performance

The absorption cycles (figure 3) were evaluated in terms of the heat and mass balance for each component with the aid of a computerized simulation program based on the thermophysical properties of the refrigerant-absorbent pairs measured and evaluated in our laboratory. With this cycle analysis, COP and  $f$  can be calculated at different temperatures of the components. The COP (based on the first law of thermodynamics) and circulation ratio,  $f$ , were calculated by:

$$COP = \frac{Q_e}{Q_g + W_p} ; f = \frac{\dot{m}_s}{\dot{m}_r} \quad (2)$$

where  $Q_e$ ,  $Q_g$  and  $W_p$  are the heat rejected from the evaporator, the heat supplied to the generator, and the energy supplied to the pump, respectively;  $\dot{m}_s$  is the mass flow rate of the strong solution (from the absorber to the generator); and  $\dot{m}_r$  is the mass flow rate of the refrigerant.

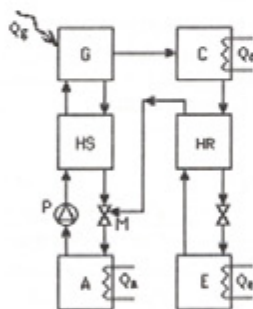


Figure 3: Schematic representation of a single-stage absorption cycle. (G - generator, A - absorber, C - condenser, E - evaporator, HR- refrigerant heat exchanger, HS - solution heat exchanger, P - solution pump, M - jet ejector).

For purposes of illustration, the absorption cycles were calculated under the following operating conditions: generator temperature of 80-140°C, evaporator temperature of -5°C, cooling water at 25°C (condenser temperature of 32°C and absorber temperature of 28°C). COP and  $f$  as functions of the generator temperature for R125-DMETEG and for R134a-DMETEG were calculated and are given in figures 4.

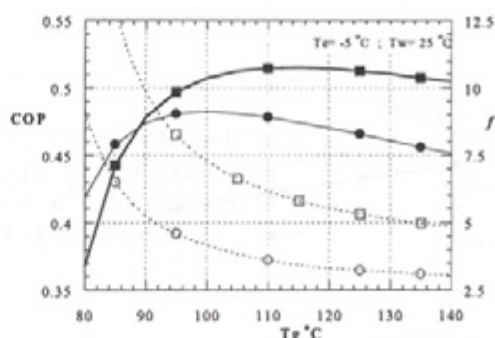


Figure 4: Variation of COP (black symbols) and  $f$  (open symbols) with generator temperature. ( - R134a-DMETEG and - R125-DMETEG).

As can be seen in figure 4 the maximum COP of 0.515 was achieved by R134a-DMETEG at generator temperature of 110-120°C while the maximum COP of 0.482 was achieved by R125-DMETEG at generator temperature of 100°C. At these ranges of generator temperature, the circulation ratio values for R134a-DMETEG were in the range of 5.5-6.2, and for R125-DMETEG were 4.1. In term of COP R134a-DMETEG has higher values but in term of  $f$  R125-DMETEG values are lower. So if the generator temperature is about 95-100°C, the R125-DMETEG is preferable, (the COP's are close, while the  $f$  values are, 4.1-4.6 for R125-DMETEG and 7.3-8.3 for R134a-DMETEG).

At these generator temperatures, the variation of COP and  $f$  with changes of evaporator temperature  $T_e$  or changes with cooling water temperature  $T_w$  are shown in figures 5 and 6.

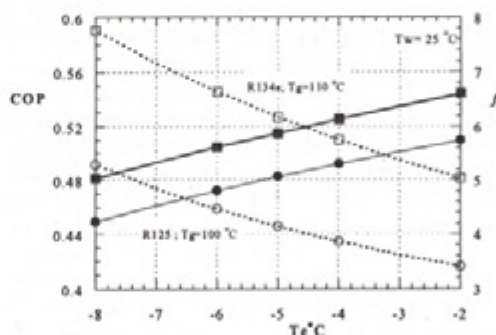


Figure 5: Variation of COP (black symbols) and  $f$  (open symbols) with evaporator temperature. ( - R134a-DMETEG and - R125-DMETEG).

The variation of the COP and the circulation ratio,  $f$  with evaporator temperature  $T_e$  can be seen in figure 5 when the cooling water temperature ( $T_w=25^\circ\text{C}$ ) and the generator temperature  $T_g$  for each of the working fluids remains constant (100°C for R125-DMETEG, 110°C for R134a-DMETEG, respectively). Reducing the evaporator temperature  $T_e$  by 5°C (from -2.5°C to -7.5°C) causes the reduction in COP's values by about 10% and increases the  $f$  values by about 45%.

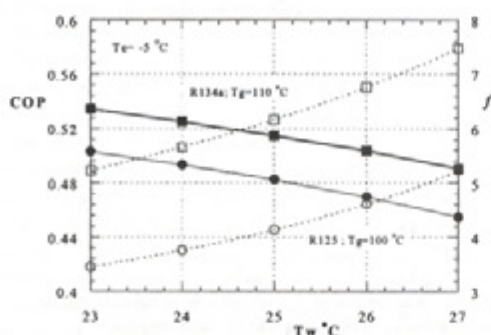


Figure 6: Variation of COP (black symbols) and  $f$  (open symbols) with cooling water temperature. ( - R134a-DMETEG and - R125-DMETEG).

The variation of the COP and the circulation ratio,  $f$ , with cooling water temperature  $T_w$  can be seen in figure 6 when the evaporator temperature ( $T_e = -5^\circ\text{C}$ ) and the generator temperature  $T_g$  for each of the working fluids remains constant ( $100^\circ\text{C}$  for R125-DMETEG,  $110^\circ\text{C}$  for R134a-DMETEG). Reducing the cooling water temperature  $T_w$  by  $4^\circ\text{C}$  (from  $27^\circ\text{C}$  to  $23^\circ\text{C}$ ) will result in increasing the COP's values by about 10% and reduction of  $f$  values by about 45%.

#### DISCUSSION AND CONCLUSION

With the aid of a computerized simulation program for a single-stage absorption cycle the performance characteristics of the working fluids R125-DMETEG and R134a-DMETEG were calculated at the same conditions and then compared. The investigation showed that a maximum value for the COP is obtained at different generator temperature depending on the working fluids. The maximum value of the COP for R134a-DMETEG was 0.515 where the generator temperature varied in the range of  $110$ - $120^\circ\text{C}$ . The maximum value of the COP for R125-DMETEG was 0.482 at generator temperature of  $100^\circ\text{C}$ .

At these generator temperatures, the circulation ratio values for R134a-DMETEG were higher than for R125-DMETEG (i.e., 5.5-6.2, and 4.1, respectively).

Although the COP values, which were obtained with the pair R134a-DMETEG, were higher than those of the R125-DMETEG, the use of the working fluids R125-DMETEG is preferable since both the circulation ratio and the generator temperature are lower. This may result in a smaller absorption refrigeration unit.

The effects of changes of the evaporator and the cooling water temperatures on the COP and the circulation ratio,  $f$ , were also examined at the generator temperatures where the COP are at maximum.

It was found that increasing the evaporator temperature,  $T_e$ , by  $2.5^\circ\text{C}$  results in increasing the COP by about 5% and in decreasing the circulation ratio,  $f$ , by about 22%. An inverse effect was obtained while changing the cooling water temperature. Increasing the cooling water temperature by  $2^\circ\text{C}$  results in decreasing the COP values by 5% and increasing the circulation ratio by about 22%.

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#### NOMENCLATURE

$COP$	-	Coefficient of performance
$f$	-	Circulation ratio ( $\dot{m}_s/\dot{m}_r$ )
$G^E$	-	Excess molar Gibbs energy
$h$	-	Specific enthalpy (kcal/kg-1)
$\dot{m}$	-	mass flow rate (kg/s)
$p$	-	Pressure (bars)
$Q$	-	Heat Source/Sink (Watt)
$T$	-	Temperature (K)
$W$	-	Work (Watt)
$x$	-	Mole fraction in liquid phase
$\xi$	-	Weight fraction in liquid phase

#### Superscripts

$E$	-	Excess
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#### Subscripts

$a$	-	Absorbent
$e$	-	Evaporator
$g$	-	Generator
$p$	-	Pump
$r$	-	Refrigerant
$s$	-	Solution