

Performance study of an absorption heat pump operating with a new working pair using group contribution method

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Abstract

The use of new working pairs for absorption heat pumps may be a new solution to avoid all negative effects towards the environment that may be caused by fluids Chlorofluorocarbons (CFC) and hydro chlorofluorocarbon (HCFC). Consequently, in this contribution the performance of absorption heat pumps (Type I and Type II) was determined using the pairs (R134a + DMA) and (R134a + NMP) as a new working pairs. The calculation of the coefficient of performance of the considered absorption cycle was based on concept of contribution of groups, such as UNIFAC. Hence, the knowledge of the thermodynamic properties of these proposed pairs, such as critical properties is necessary for the prediction of equilibrium liquid-vapor and enthalpy. The best refrigerants will be selected according to the COP value.

Finally, the approach led to interesting performance results for the tested pairs, comparable and close to those for existing working fluid pairs.

Keywords: Refrigerants, absorption heat pumps, thermodynamic properties, COP, equilibrium liquid-vapor, enthalpy, contribution of group, UNIFAC.

I. Introduction

Despite their good performance and physical properties when used as refrigerants in compression heat pumps, Chlorofluorocarbons (CFCs) and Hydro Chlorofluorocarbons (HCFCs) have been banned due to their negative impact towards the environment, particularly the ozone layer. This has encouraged the search for substitutes and their replacement by HFCs (Hydro Fluorocarbons) or by natural fluids such as ammonia. These do not have a negative impact on the ozone layer but they also have disadvantages for the natural environment in certain situations, such as the greenhouse effect, acidification ... etc. In addition to the environmental problems recorded in the heat and/or cold industry,

the energy consumption has also a great influence from an economic point of view.

Nowadays there are more than 130 million heat pumps installed in industry and in the residential and tertiary sectors. The market has become important with millions of pumps sold every year in different parts of the world [1]. This is becoming even more important due to the economic development of many populated countries and to the continuous growth in industrialized countries, hence increased energy consumption.

Among the most effective means for energy conservation and environmental protection are the adsorption machines, which can promote lost heat (industrial or other). They may also use refrigerants as working fluid pairs (refrigerant/absorbent), for

their operation without any adverse effects on the environment.

In fact the absorption heat pump system is considered one of the most environmentally friendly means of heating towards air, soil or water.

Generally two types of absorption heat pumps are used, Lithium bromide (Type I) and Ammonia (Type II). The following table shows the main advantages and disadvantages of these two pairs:

Refrigerant/absorbent	Advantages	Disadvantages
NH₃/Water	Low corrosion	High toxicity. High pressure. Need for a distillation column. Complex and expensive facilities.
Water/LiBr	Excellent material transfer and heat performance. Non volatility of the absorbent. Low toxicity.	High corrosion Low solubility. Crystallization of the high concentration absorbent in the absorber.

For that reason, various researchers are lunched based on absorption cycles where the available waste heat can allow stimulating the investigation and test of new working pairs. The performance (COP) depends mostly on the substances used as working pair. Therefore it is important to know the influence of the thermodynamic properties of the pure component on the performance of an absorption heat cycles.

Assessing the working pairs with the thermodynamic method is an effective way to shorten the developing period. The conventional methods to evaluate working pairs are through analysing the influences on the absorption cycle caused by the physical and chemical properties of pure component of the working pairs [2].

Generally, in the majority of the studies achieved on the absorption systems, the choice of the good refrigerants couple depends on the values reached for some keys parameters as the coefficient of the performance COP, the rate of circulation as well as the levels of pressure imposed by the temperatures of change of phases of the refrigerant couple and the molar fractions of this last. However some other properties, as the properties of excess could be of an importance no negligible for the choice of the refrigerants couple.

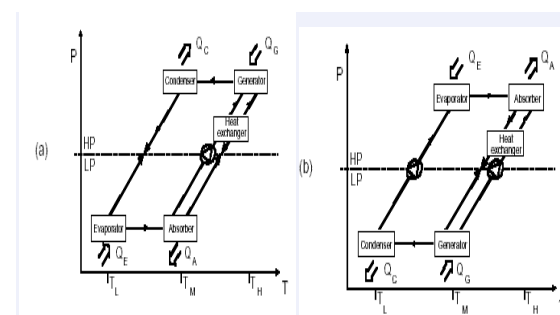
In this work, the survey of the performance of absorption cycle (Type I and Type II) using some organic working pairs as 1,1,1,2-tetrafluoroethane(R134a)/NN, Dimethylacetamide

(DMA) et R134a/N-methyl-2 pyrrolidone (NMP), was considered.

According to the thermodynamic analysis of an absorption heat pump cycle, a systematic research on some new working pairs were launched, starting with some organic compounds. For the evaluation of the properties of mixture, methods based on the concept of contribution of groups, as the UNIFAC, are used.

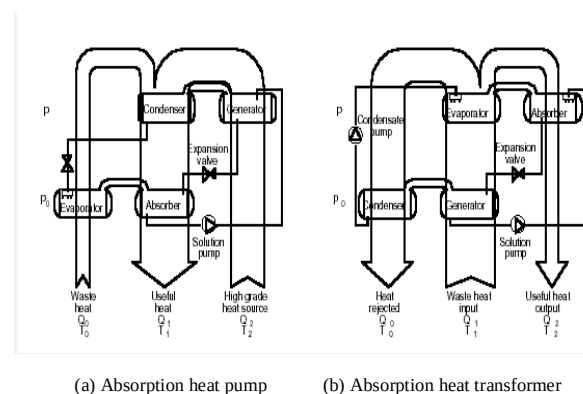
II. Cycle Description:

The absorption heat pump (AHP) requires a high-grade energy source, in this case high temperature (T_H) heat to upgrade a low-grade source (T_L). Two or more units of useful medium-grade energy (T_M) are obtained for every unit of high-grade heat put in. The absorption heat transformer (AHT) takes intermediate-grade heat and converts about half of it to high-grade heat and rejects half as low-grade heat. Figure 2 shows the plant schematics and energy flows for AHTs and AHPs. The working cycles for AHPs and AHTs are explained below, with reference to Figure 1. and Figure 2. The two cycles have quite different thermodynamic characteristics, as illustrated in Figure 3, and hence different applications [3].



(a) Principal diagram of the absorption heat pump cycle. (b) Principal diagram of the absorption heat transformer cycle

Figure 1: Absorption heat pump and heat transformer cycles (CADET, 1989).



(a) Absorption heat pump

(b) Absorption heat transformer

Figure 2: Plant schematics and heat flows for absorption heat pumps and transformers (Linton, 1993)

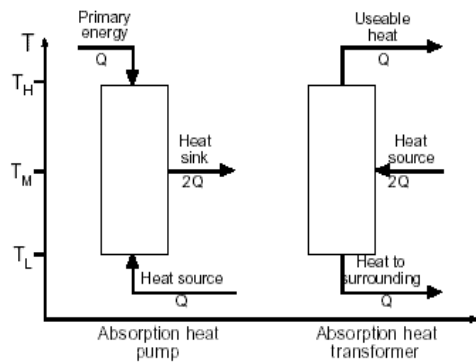


Figure 3: Absorption heat pumps and transformers (CADET, 1989)

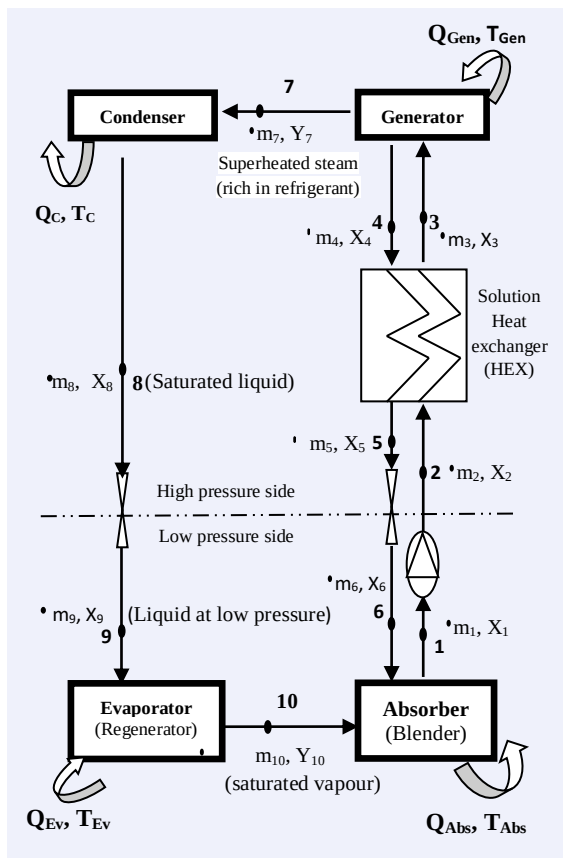


Figure 4: Single stage of an absorption heat pump

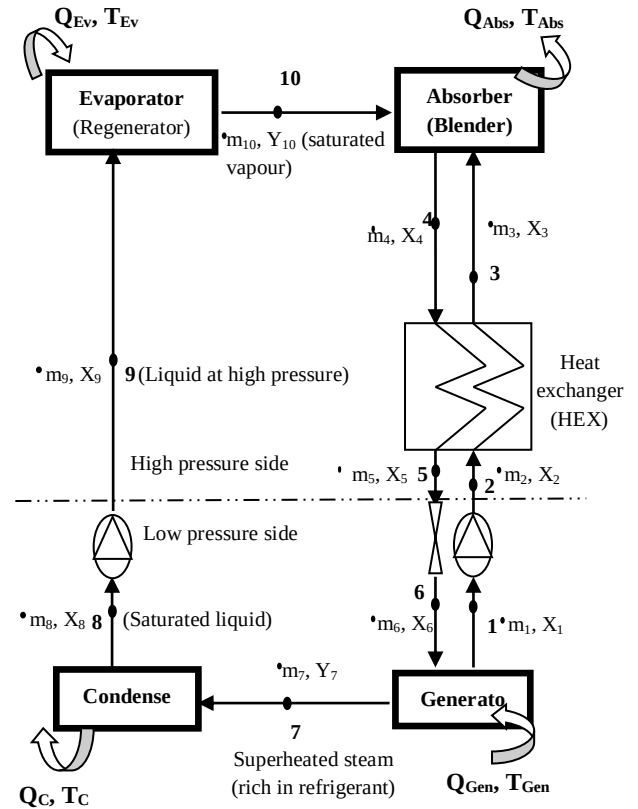


Figure 5: Single stage of an absorption heat Transformer

Schematically, Figure 4 and 5 shows that a single stage AHP and AHT consists of a generator G, an absorber A, an evaporator E, a condenser C, a heat exchanger HEX, pumps P_s and P_c , and throttle V_s . The difference between the two configurations is a difference in the pressure level in the four main heat exchangers (the evaporator, absorber, generator and condenser), which affects the temperature levels of the heat streams [4].

With an AHT, the working solution is in the generator and is heated by the waste heat stream (Q_G at T_M), an external, medium-grade heat source. Some of the resulting refrigerant evaporates and is then condensed in the condenser. Low-grade heat is rejected from the condenser (Q_C). The liquid refrigerant is then pumped to an evaporator, where it is evaporated at high temperature and pressure. More medium-grade heat (Q_E) from the waste heat stream is used to achieve this. The refrigerant vapor is then absorbed into the absorbent, which has been pumped from the generator. Heat is rejected from the absorber (Q_A) at a higher temperature (T_H) than that used in the generator. This is the usable or upgraded heat. The cycle is completed by returning the working fluid to the generator [3].

III. Methodological approach

In order to apply the principles of thermodynamics to a real cycle as represented in the figure 4& 5, some simplifications on the working of this one were considered in deriving some hypotheses.

The working pairs of the absorption cycle are the non-ideal solutions. Usually, their vapor-liquid equilibria has some negative deviations from the Raoult's law. In the systems with the negative deviations from the Raoult's law, the activity coefficient γ_i is above 1 for each component.

$$\ln \gamma_i = f(T, x_1, x_2, \dots, x_N) \quad (i = 1, 2, \dots, N) \quad (1)$$

A relation (1) shows that the activity coefficient model depends on the system temperature and all component compositions and, to lesser extent, the total pressure. It is related to the excess Gibbs function (G^E), equation (2.1).

$$G^E(T, P, x) = \sum_{i=1}^N x_i \left[\frac{\partial(nG^E)}{\partial n_i} \right]_{T, P, n_{j \neq i}} \quad (2)$$

$$G^E(T, P, x) = RT \sum_{i=1}^N x_i \ln \gamma_i \quad (2.1)$$

The cycle simulation is based on the mass balance, energy balance and phase equilibrium for each compartment of the cycle. These equations are written:

$$\sum_i m_i = 0 \quad (3)$$

$$\sum_i h_i m_i + \sum_i Q_i + \sum W = 0 \quad (4)$$

$$f(T, P, x_i) = 0 \quad (5)$$

III.1. Thermodynamic model

For a simulation of an absorption heat pump cycle, several pure component properties for the refrigerant as well as for the absorbent must to be known. The most important are the critical proprieties, acentric factor etc. We need also to determine the activity coefficient.

The investigation of the influence of various thermodynamic properties on the performance of absorption heat pump necessitates a reliable method of simulating the heat pump cycle. Justly in this work we chose a group contribution method, specially UNIFAC, this method proved to be

powerful tools to estimate vapor-liquid equilibria for various chemical engineering purposes. The idea behind these methods is to deduce the behavior of a mixture from interactions between functional molecular groups which build up the molecules of the constituent mixtures [5].

The required interaction parameters for the functional groups are fitted to a great number of experimental data. We chose UNIFAC method as the base for the screening also, for reason of greater versatility and better data access.

IV. Criteria:

IV.1. Coefficient of performance (COP):

For AHP (Figure 4) the cycle COP is expressed as follow:

$$COP = \frac{Q_E}{Q_G + W} \quad (6)$$

For AHT (Figure 5) the cycle COP is defined as the ratio of the benefit heat obtained to the driving energy required as follows:

$$COP = \frac{Q_A}{Q_E + Q_G + W} \quad (7)$$

IV.2 Temperature lift ($\Delta\theta$)

The temperature lift $\Delta\theta$ represent the difference between the available temperature T_H and the heat source temperature T_M . This parameter shows that the greater the $\Delta\theta$, the more powerful the machine [6].

IV.3 Circulation ratio (C_R)

The circulation ratio is defined as the ratio of the mass flux of the rich solution needed to the ratio of the absorbate vapor produced in the cycle [7 & 8].

$$\text{For AHP } C_R = \frac{m_6}{m_{10}} \quad (8)$$

$$\text{For AHT } C_R = \frac{m_3}{m_{10}} \quad (9)$$

The C_R is a economic significance parameter. To increase the C_R means to increase the operating cost and equipment investigation.

Therefore, to get the biggest COP and higher $\Delta\theta$ with the smallest C_R is an engineering pursuit.

The coefficient of performance is expressed in terms of the energy balance in the cycle

quantitatively. So in basing on the energy balance and mass balance the expression of COP become:

For AHP:

$$COP = \frac{h_{10} - h_9}{(1 + C_R)(h_1 - h_6) + (h_7 - h_6) + W} \quad (10)$$

For AHT:

$$COP = \frac{C_R h_3 + h_{10} - (1 + C_R) h_4}{C_R h_1 + h_7 - (1 + C_R) h_6 - h_9 + h_{10} + W} \quad (11)$$

V. Results and discussion

In order to carry out our study, which consists in testing new working pairs (refrigerant/absorbent) on an absorption heat pump, it was necessary to select refrigerant - absorbent couples (Table 1). The essential for these couples, that the absorbent must have a sufficiently high boiling point to ensure a good separation of the refrigerant, and in return the refrigerant must also have a high solubility in the solvent (absorbent).

Table.1: Studded working pairs (Refrigerants/Absorbents)

	Constituents	Formula	UNIFA group decomposition
Refrigerants	R134a	$C_2H_2F_4$	1CF ₃ ; 1CF
Absorbents	DMA (NN,dimethylactamide)	C_4H_9NO	1CH ₃ ; 1HCON(CH ₃) ₂
	NMP (N-methyle-2 pyrrolidone)	C_5H_9NO	1CH ₃ :1CH ₂ ; 1HCON(CH ₂) ₂

The most important proprieties needed to simulate the heat pump cycle was grouped in the following tables:

Table.2: Critical and acentric factor properties [9]

Constituents	M g/mol	Tb K	Tc K	Pc Bar	Vc cm ³ /mol	ω
$C_2H_2F_4$ (R134a)	102.03	247.15	374.3	40.64	201	0.32669
DMA	87.12	439.25	658.0	40.30	321	0.363509
NMP	99.13	477.42	721.8	47.80	310	0.395027

Table.3: UNIFAC interaction Parameters [9]

Groups	CF ₃	CF	CH ₃	CH ₂	HCON(CH ₂) ₂	HCON(CH ₃) ₂
CF ₃	0	0	147.30	147.30	55.8	55.8
CF	0	0	147.30	147.30	55.8	55.8
CH ₃	-2.859	-2.859	0	0	485.3	485.3
CH ₂	-2.859	-2.859	0	0	485.3	485.3
HCON(CH ₂) ₂	-5.579	-5.579	-31.95	-31.95	0	0
HCON(CH ₃) ₂	-5.579	-5.579	-31.95	-31.95	0	0
Q _K	1.3800	0.4600	0.8480	0.5400	2.120	2.736
R _K	1.4060	0.6150	0.9011	0.6744	2.6322	3.0856

Because the most important parameter for a good performance of an absorption cycle are: coefficient of performance COP, circulation ratio C_R and temperature lift $\Delta\theta$. The influence of each of the last two parameters on the performance of the cycle was taken in consideration.

V.1. Absorption heat pump (Type I):

- (R134a + DMA) working pairs :

The obtained results are illustrated as follows:

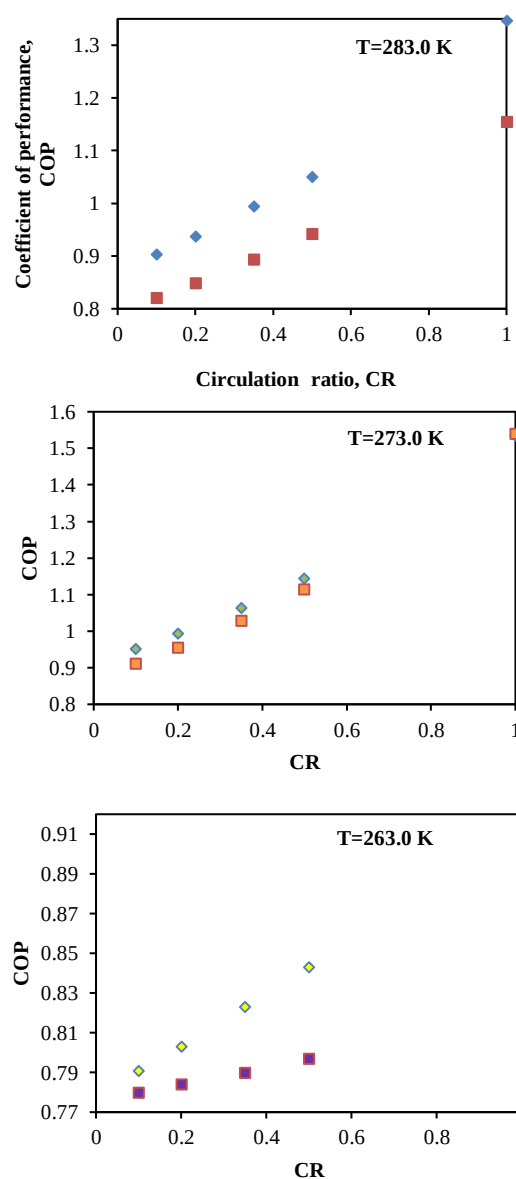


Figure 1: Effect of circulation ratio on the coefficient of performance COP of (R134a+DMA) working pairs,

at the temperature 283 K : $\Delta\theta=11.79$ (bleu), $\Delta\theta=17.39$ (red) and $P_{Gen}=1.2$ bar, $P_{abs}=0.24$ bar.

At T= 273 K : $\Delta\theta=11.39$ (Green), $\Delta\theta=22.39$ (orange) and $P_{Gen}=1.07$ bar, $P_{abs}=0.35$ bar.

At T=263 K : $\Delta\theta=12.59$ (yellow), $\Delta\theta=23.79$ (violet) and $P_{Gen}=1.1$ bar, $P_{abs}=0.24$ bar.

- (R134a+NMP) working pairs:

The obtained results are illustrated as follows:

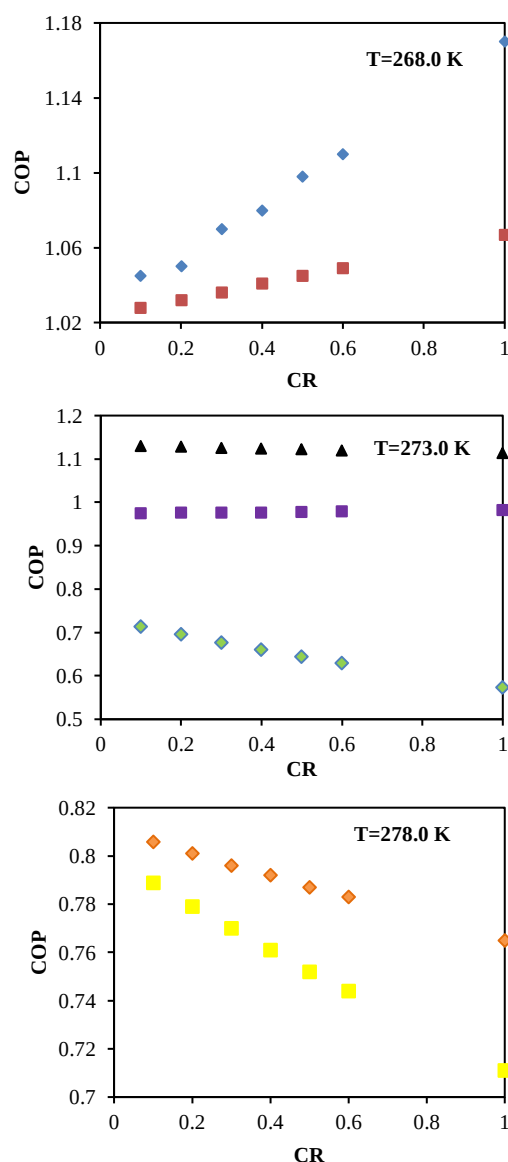


Figure 2: Effect of circulation ratio on the coefficient of performance COP of (R134a+NMP) working pairs,

At T= 268 K : $\Delta\theta=18.79$ (Bleu), $\Delta\theta= 28.19$ (Red) and $P_{ev}= 0.31$ bar, $P_{abs}= 1.01$ bar.

At T=273 K : $\Delta\theta=12.59$ (Green), $\Delta\theta= 21.79$ (Violet), $\Delta\theta= 57.79$ (black) and $P_{ev}=0.64$ bar, $P_{abs}= 1.39$ bar.

At T=278 K : $\Delta\theta=11.39$ (Orange), $\Delta\theta= 22.99$ (Yellow) and $P_{ev}= 0.76$ bar, $P_{abs}=1.81$ bar.

V.2. Absorption heat transformer(AHP - Type II or AHT) :

The obtained results are illustrated as follows:

- (R134a+ DMA) working pairs :

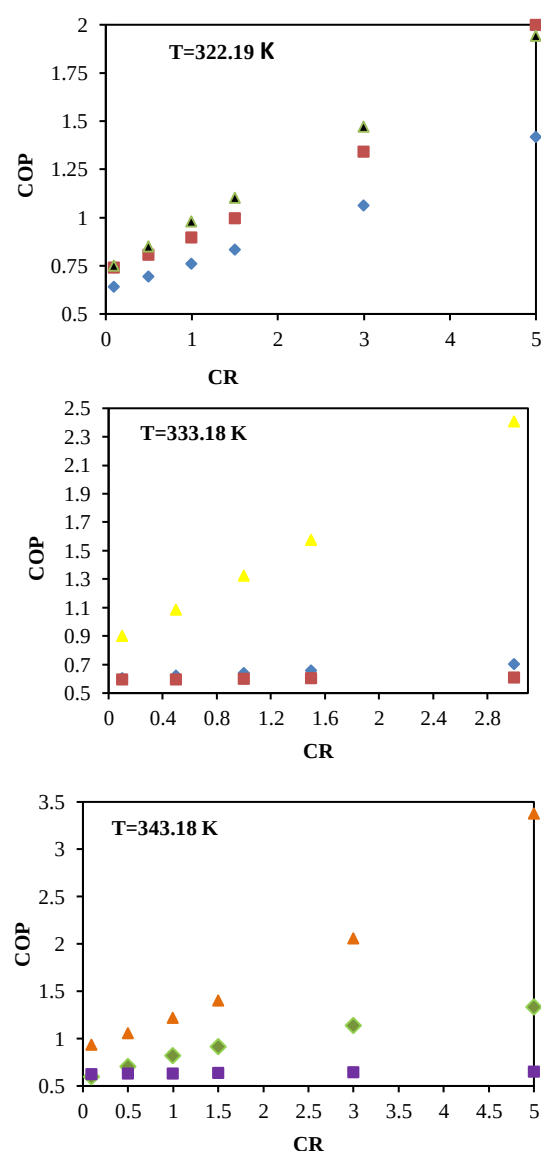


Figure 3: Effect of circulation ratio on the coefficient of performance COP of (R134a+DMA) working pairs,

At T = 322.19 K: $\Delta\theta=11.4$ (Bleu), $\Delta\theta= 22.4$ (Red), $\Delta\theta= 31.4$ (Black) and $P_{Gén}=1.4$ bar, $P_{abs}= 1.896$ bar.

At T=333.18 K : $\Delta\theta=12.01$ (Bleu), $\Delta\theta= 21.6$ (Res), $\Delta\theta= 33.6$ (Yellow) and $P_{Gén}=1.16$ bar, $P_{abs}= 1.77$ bar.

At T= 343.18 K : $\Delta\theta=13.21$ (Green), $\Delta\theta= 23.61$ (Violet), $\Delta\theta= 29.61$ (Orange) and $P_{Gén}=1.42$ bar, $P_{abs}= 2.16$ bar.

- (R134a+NMP) working pairs :

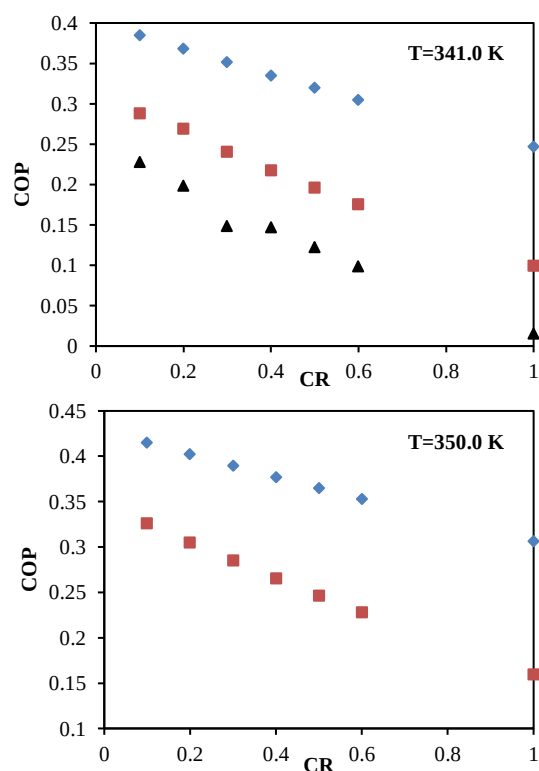


Figure 4: Effect of circulation ratio on the coefficient of performance COP of (R134a+NMP) working pairs;

T=341 K : $\Delta\theta = 14.59$ (Bleu), $\Delta\theta = 25.99$ (Red), $\Delta\theta = 31.99$ (Black) and $P_{Gén}=0.71$ bar, $P_{abs}= 1.4$ bar.

At T=350 K : $\Delta\theta = 09.19$ (Bleu), $\Delta\theta = 19.59$ (Red), and $P_{Gén}= 0.84$ bar, $P_{abs}= 1.71$ bar.

It should be noted that the circulation ratio value of the solution must be as low as possible, so as to reduce the power absorbed by the pump, and that more ($\Delta\theta$) is large, the absorption machine is powerful.

The figures below above show the evolution of COP as a function of CR and $\Delta\theta$ where it can be noted that the COP values of absorption heat pumps, type I and II, using (R134 a+DMA) working pairs are generally higher than those using (R134 a+NMP) working pairs, especially for AHP - type II.

VI. Conclusions

The main conclusions of this work are the following: Using, (R134a+DMA) and (R134a + NMP) working pairs on the performance of the (A.H.P) cycle.

The binary systems studied in this work, are results more or less comparable to the values of the performance coefficients of existing heat transformers, where H2O-LiBr is used as an active fluid and where the performance coefficient of the

majority of heat transformers varies from 0,45 to 0,49 [10].

The two cases: easy to absorb but difficult to separate for every working pairs or inversely, have for consequence to decrease the performance of the considered absorption cycle.

The model of general thermodynamics analysis used during this contribution is based on the method of group contribution, conceived for the prediction of thermodynamic properties and the test of performances. The reliability of this method, already proven by the previous studies, has been demonstrated again.

Finally, results of this survey can be developed more, seen the present importance of absorption machines. As it would be interesting to consider exergetic approach that includes the first and the second principle of the thermodynamics. That means to calculate with precision consequences of the various thermodynamic irreversibility phenomena.

VII. List of symbols

AHP	Absorption heat pump
AHT	Absorption heat transformer
COP	Coefficient of performance
C_R	Circulation ratio
G^E	Excess Gibbs free energy ($J.mol^{-1}$)
H	Enthalpy ($J.Kg^{-1}$)
H^E	Excess enthalpy ($J.mol^{-1}$)
m	mass flux ($Kg.h^{-1}$)
n	number of molars (mol)
p	pressure (Pa)
Q	heat flux ($J.h^{-1}$)
R	universal gas constant, $8.318 J.mol^{-1}.K^{-1}$
T	Temperature (K)
W	work flux ($J.h^{-1}$)
x_i	mol fraction of component i
x_R	concentration of rich solution
x_P	concentration of poor solution

Greek letters

$\Delta\theta$ Temperatures lift (K)

γ_i Activity coefficient

Subscripts

A absorber
C condenser
E evaporator
G generator
H high temperature level
L low temperature level
M intermediate temperature level

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