Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Thermal Sciences 42 (2003) 631–638

International Journal of Thermal Sciences

www.elsevier.com/locate/ijts

Experimental study of an innovative absorption heat transformer using partially miscible working mixtures

Dominique Alonso [a,b,*], Thierry Cachot [a,b], Jean-Marie Hornut [a,b]

[a] *LSGC-CNRS-ENSIC, 1, rue Grandville, BP451, 54001 Nancy cedex, France*
[b] *IUT Nancy Brabois Le Montet, Université Henri Poincaré, 54601 Villers-lès-Nancy cedex, France*

Received 21 March 2002; accepted 31 August 2002

Abstract

Absorption heat pumps are a suitable solution for a rational use of waste heat. In this field of application, absorption heat transformers can use low temperature level heat to produce useful thermal energy at higher temperature level. Nevertheless, their performances are still limited, which leads to too long payback periods. This article describes the principle of an innovative heat transformer cycle using a working mixture partially miscible at low temperature. Hence, the separation step, classically done by distillation in absorption heat pump, is replaced by an energy costless one obtained by simply cooling down the mixture. Results of the operation of a laboratory scale pilot unit are presented. The machine operating over the *n*-heptane–DMF mixture has allowed to observe a 8 °C temperature lift with thermal efficiency varying from 30 to 40%. Hence, the practical feasibility of such a cycle has been demonstrated.

Keywords: Partial miscibility; Heat pump; Absorption; Heat transformer

---

1. Introduction

Industrial waste heats are a huge source of driving heat for absorption heat pumps (AHP) and especially absorption heat transformers (AHT). This last cycle allowing to produce useful heat (high temperature level heat) from a costless source, makes it really useful for a rational use of energy, since it allows to decrease the amount of primary energy (fossile fuels for example) consumed. Nevertheless, AHT are rarely used in practice. Their performances remain low (only 30 to 50% of the driving–waste–heat is effectively upgraded to an interesting temperature level [1]). Those low quantitative performances lead to long payback periods. Moreover, technical limitations such as corrosion problems (mainly for machines using the water/lithium bromide working pair) or crystallization limit the temperature lift and the temperature range of utilization of AHT [2]. Important efforts to propose new working fluids or multistage structures have still not allowed to widespread this technology.

Thanks to exergy analysis, it has been possible to establish that the separation step in absorption heat pumps, which is obtained by rectifying the working mixture, was the main contribution to the exergy destruction in absorption cycles [3]. Thus, this lead us to consider other ways (less exergy destructive) to separate the working mixture components. Following an idea suggested many years ago by several authors [6,7], mainly for absorption chillers [5,9], we propose to use a partially miscible mixture as a working pair. In such a heat transformer cycle, a partial miscibility at low temperature is required [4,10]. Hence, the working mixture has only to be cooled down to a temperature lower than the upper critical solution temperature (UCST) to separate into two liquid phases respectively rich in absorbent and in refrigerant. This solution also allows to operate the whole cycle under a single working pressure.

Seemingly, no experimental work has been realized on this type of absorption cycle. So, the aim of our study was to build a laboratory scale heat transformer pilot using a partially miscible pair in order to validate the technical feasibility of the new cycle and the influence of operating parameters.

---

[*] Corresponding author.
E-mail address: dominique.alonso@ensic.inpl-nancy.fr (D. Alonso).

1290-0729/03/$ – see front matter
doi:10.1016/S1290-0729(03)00028-0

Nomenclature

AHP	absorption heat pump	
AHT	absorption heat transformer	
COP	coefficient of performance	
DMF	N,N dimethylformamide	
F	molar flowrate	$\text{mol}\cdot\text{s}^{-1}$
g^M	molar enthalpy of mixing	
HE	heat exchanger	
J	molar feed ratio	
LLE	liquid–liquid equilibrium	
L_v	latent heat of vaporization	$\text{J}\cdot\text{mol}^{-1}$
PP	polypropylene	
PTFE	polytetrafluoroethylene	
PU	circulation pump	
Q	heat flow	W
RRC	reverse rectification column	
T	temperature	°C
UCST	upper critical solution temperature	
V	valve	
VLE	vapor–liquid equilibrium	
x	refrigerant mole fraction	

Subscript

ABS	absorber
COL	column
COO	cooler
EVA	evaporator
loss	heat loss
SET	settler

Greek letters

ΔT_i	internal temperature lift	°C
η_{th}	thermal efficiency	

2. Principle of the absorption-demixing heat transformer cycle (ADHT)

2.1. Classical AHT cycle

An absorption heat transformer consists mainly on five elements (Fig. 1): a generator, a condenser, an evaporator, an absorber and a heat recovery heat exchanger. The working mixture is composed by a low boiling component, the refrigerant, and a leaner one, the absorbent. Low grade (waste) heat is supplied to the generator to boil off the refrigerant. The produced vapor flows in the condenser cooled down at ambient temperature. The liquid refrigerant and the absorbent rich solution coming from the generator are then pumped to a higher pressure. Low grade heat (at the same temperature then the heat supplied to the generator) is used to vaporize the refrigerant (in the evaporator). Upgraded heat is delivered in the absorber by absorbing the refrigerant vapor in the absorbent rich solution. The produced mixture is returned to the generator after throttling and a new cycle can start again. The heat recovery heat exchanger is used to preheat the solution coming from the generator and to cool down the mixture before throttling.

2.2. The ADHT cycle

2.2.1. Partial miscibility

The stability condition for a binary liquid mixture is obtained when its Gibbs energy is minimal. This condition can be expressed in term of molar Gibbs energy of mixing [8] (Eq. (1)):

$$\frac{\partial g^M}{\partial x} > 0 \tag{1}$$

When the mixture is composed of structurally different compounds (in shape or polarity), it is possible to observe for some temperatures a molar Gibbs energy behavior with composition described by Fig. 2. Mixtures with compositions between x_A and x_B are thermodynamically unstable. They split into two liquid phases of respective composition x_A and x_B.

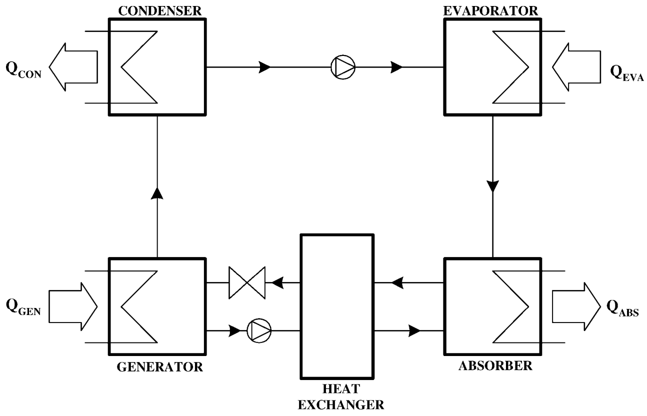

Fig. 1. Schematic diagram of a classical AHT cycle.

Temperature has an influence on this liquid phase splitting. The mixtures used in ADHT present a miscibility gap under a determined temperature called upper critical solution temperature (UCST). Above this temperature the mixture is fully miscible. On Fig. 3, the solid line curve delimits the miscible and immiscible zones. It also allows to determinate the composition, x_A and x_B of the liquid phases in equilibrium at a temperature T.

2.2.2. Basic concept

The innovation in this absorption cycle is the use of a mixture which exhibits a miscibility gap at low temperature. The working mixture is cooled down under the UCST by a low temperature heat sink (ambient air or river water for example) and splits into two liquid phases. This separation step occurs in the settler (Fig. 4). The refrigerant rich phase

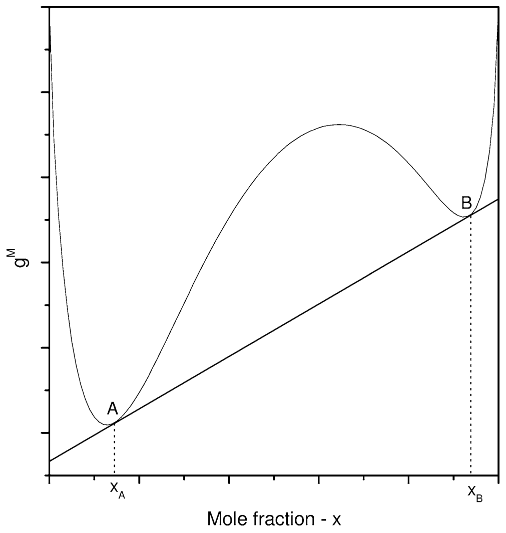

Fig. 2. Molar Gibbs energy of mixing for immiscible mixtures.

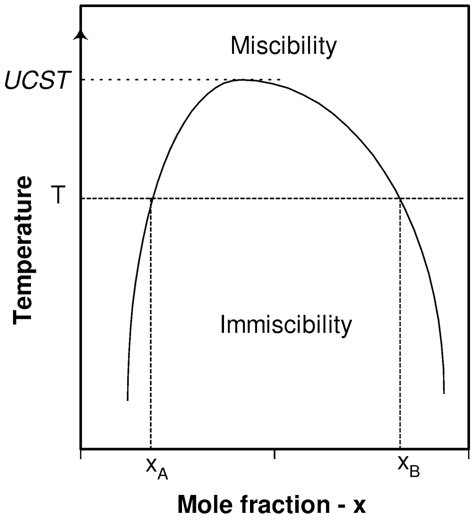

Fig. 3. Liquid–liquid equilibrium curve.

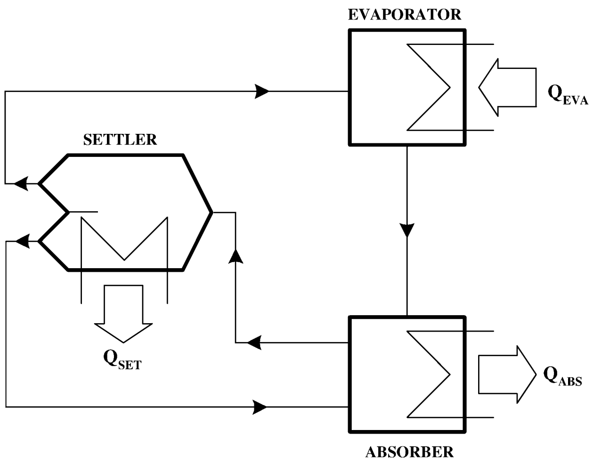

Fig. 4. Schematic diagram of the basic ADHT cycle.

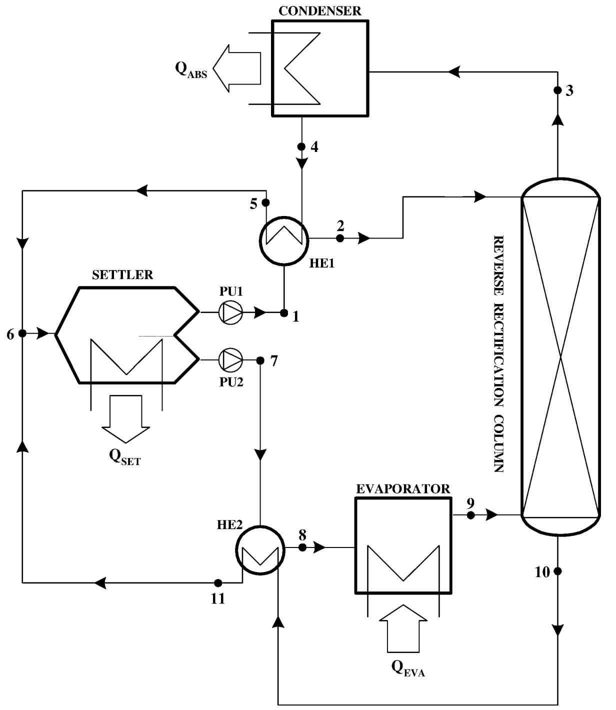

Fig. 5. Schematic diagram of the improved ADHT.

is then vaporized and absorbed in the absorbent rich phase. Apart from the energetically costless separation step, this cycle also present the advantage to be simpler than the classical AHT one. The generator and condenser of the AHT are replaced by a simple cooled settling vessel in the ADHT. This can lead to interesting reduction on the investment costs and consequently on the pay-back period. The possibility to operate the whole cycle under a single pressure level also allows to reduce the cost of pumping and throttling devices.

2.2.3. *An improved ADHT cycle*

As well as in conventional AHT cycles, it is possible to add internal heat exchangers to the cycle in order to save energy (Fig. 5). Moreover, in the machine we propose, the absorption step is realized in a counter-current (packed or plate) column [11]. The refrigerant rich vapor is introduced at the bottom and the absorbent rich solution at the top. Upgraded heat is recovered by condensing the vapor flowing out the top of the column. This way to operate the absorption step is called reverse rectification [13] and allows to realize the absorption in a more reversible way and to reach higher temperature lift (difference of temperature between the waste heat and the upgraded heat). This improved ADHT cycle is represented in the temperature-composition diagram on Fig. 6.

2.3. *Possible applications of ADHT*

ADHT are before all AHT. They should be used for the same type of applications. We could cite the following:

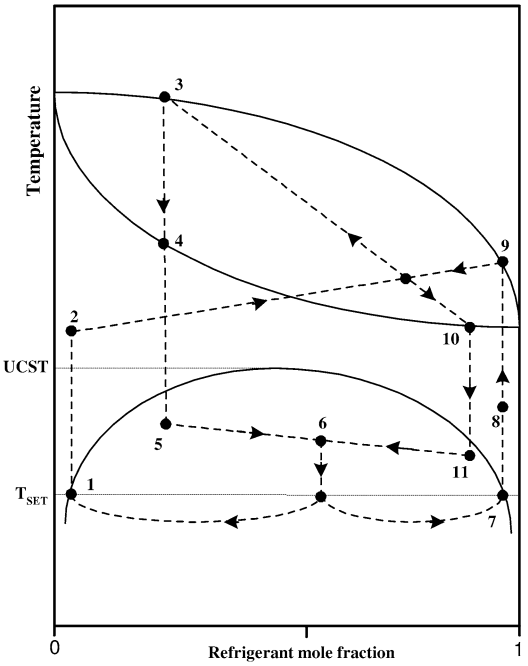

Fig. 6. The ADHT cycle in the temperature-composition diagram.

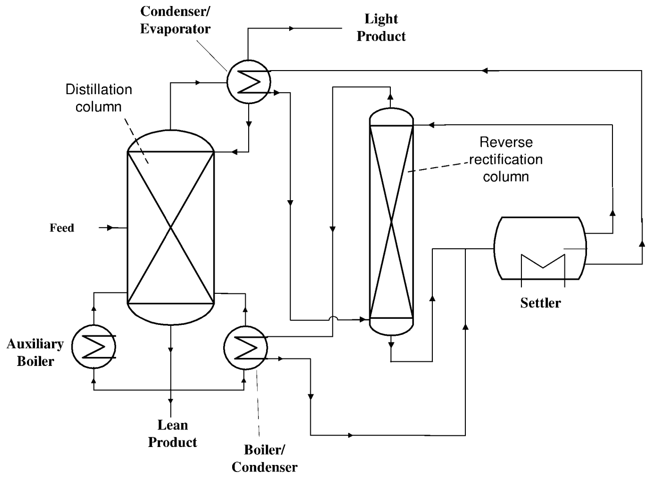

Fig. 7. Thermal coupling of an ADHT with a distillation column.

- Production of steam with hot waste water from steel mills;
- Production of hot water for district heating from geothermal water or exhaust gases of an incineration plant;
- thermal coupling of the boiler and the condenser of distillation units;
- ....

Fig. 7 represents a distillation column coupled with an ADHT. The heat available from the condenser of the distillation column is used to heat the evaporator of the ADHT. The upgraded heat is used to heat the boiler of the column. Off course, it is still necessary to provide to the boiler a relatively low amount of high temperature heat.

3. Experimental realization

3.1. Choice of the working mixture

The pilot plant built has been designed to operate in a laboratory, so safety constraints must be respected. Hence, the working mixture must be chosen so that the ADHT can be operated under atmospheric pressure and be the less toxic and explosive as possible.

The chosen working mixture is n-heptane/N,N-dimethyl formamide (DMF). This mixture presents a miscibility gap relatively large with a UCST of 73.8 °C (Quitzsch [14]). Moreover, under atmospheric pressure, liquid–liquid equilibrium (LLE) and vapor–liquid equilibrium (VLE) curves do not intersect (Zemlyanskaya [15]) which allows the absorption. Finally, the boiling points of both compounds are relatively far from each other (98.4 °C for n-heptane and 152.0 °C for DMF), which allows to obtain a temperature lift that can be experimentally observed. Simulation results (Alonso [12]) have showed that with this mixture it is possible to obtain temperature lifts up to 10 °C.

For a given working mixture, it exists a maximum value of ΔT_i. Roughly speaking, the exiting vapor at the top of the absorption column is, in the better case, in equilibrium with the absorbent rich solution inlet. This determines the maximum temperature of the exiting vapor and consequently the temperature level of the upgraded heat. Consequently, to increase ΔT_i, it is necessary to improve the separation step, which means to widen the miscibility gap at low temperature. Unfortunately, the width of this gap is only determined by the nature of the liquid–liquid equilibrium at low temperature. There are mainly three solutions to increase the phase splitting:

- Find a mixture with a wider miscibility gap;
- Decrease the settling temperature. But, this temperature is determined by the low temperature heat sink used by the ADHT;
- Add a third component to the mixture in order to modify the liquid–liquid equilibrium in the desired way.

It is noticeable that we have been able to find by numerical simulation other working mixtures that can lead to interesting temperature lifts (>50 °C). These mixtures could not be used for our experimental unit because we would have to operate it under pressures higher than the atmospheric one.

3.2. Description of the pilot plant

The experimental pilot unit is schematically represented on Fig. 8.

It is noticed that DMF is an excellent solvant of many polymers and reacts with some metals (copper, tin and their alloys). So, the materials used for the pilot plant will be glass, stainless steel, polypropylene (PP) and polytetrafluoroethylene (PTFE).

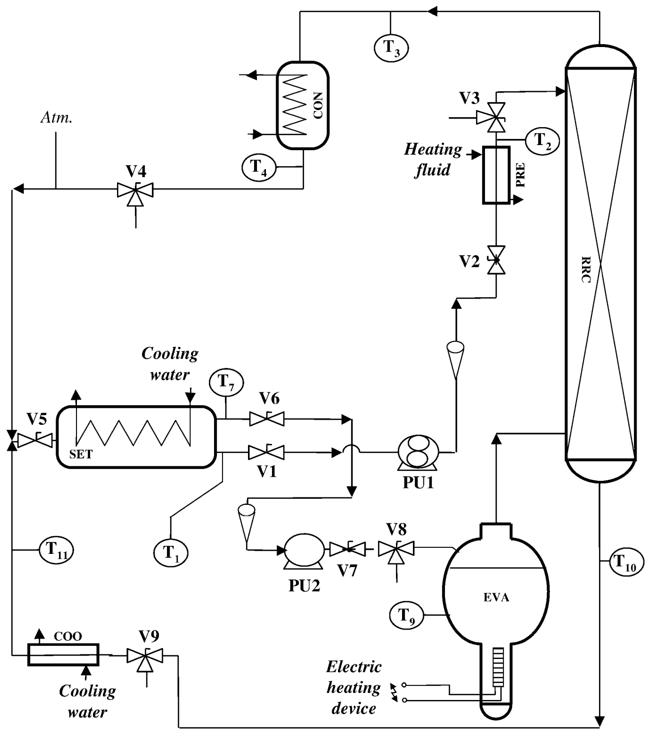

Fig. 8. The ADHT pilot unit.

3.2.1. Settler

This apparatus has two functions: cool the mixture to the settling temperature and allow the two liquid phases to segregate totally. It has been designed as a 15 L stainless-steel horizontal cylindrical drum with one inlet and with two superposed outlets on the opposite side. The average residence time of the mixture is then about 15 minutes. A transparent glass pipe connected to the drum allows to visualize the interface between the two liquid phases. Cold water circulates through a stainless steel coil pipe (exchange area: 0.05 m^2) which is immersed into the mixture to cool it down.

3.2.2. Evaporator

It is destinated to vaporize the refrigerant rich phase produced by the settler. Heat supply is normally waste heat. To control more easily and precisely the amount of heat supplied to the experimental evaporator electrical heating has been chosen. The evaporator is a spherical glass boiler (capacity: 2 L) with, on its bottom part, a cylinder containing the electrical heating device (3 kW).

3.2.3. Reverse rectification column

The mixture of the refrigerant rich vapor with the absorbent rich liquid is carried out in a counter-current packed column. Considering the vapor flowrates used for experimentations, the use of a 50 mm diameter column and multi-knit packing allows to operate on the loading zone of the column and consequently ensure a good contact between liquid and vapor phases. The height of the column has been chosen to 1.5 m to ensure that it is equivalent to 1 or more theoretical equilibrium stages.

3.2.4. Condenser

It allows to recover the upgraded heat by condensing the vapor from the top of the column. In the pilot unit, it is a vertical glass tubular element with a coil pipe (exchange area: 0.05 m^2) for the counter-current cooling water circulation.

3.2.5. Heat exchangers

To reach better performances, industrial heat transformers are equiped with heat-recovery heat-exchangers that allow to preheat the inlets of the absorber with the outlets. The preheating of the absorbent rich solution is particularly important. To study the influence of this preheating, the heat-recovery heat-exchanger corresponding to HE1 on Fig. 5, has been replaced, for the experimental ADHT, by a stainless steel tubular heat exchanger (exchange area: 0.01 m^2) fed with a heat carrier fluid (therminol oil) heated by a circulating-thermostatic bath.

The bottom outlet of the column (flow 10 on Fig. 5) is cooled in a horizontal heat exchanger identical to the condenser fed with cold water.

3.2.6. Instrumentation

Temperature measurements are done with type-K thermocouple. The precision of the measure is 0.5 °C.

Compositions of the flow on the different points of the cycle have been determined by an off-line gas chromatography analysis (a Porapak QS column has been used). This analysis have been realized on samples obtained during the operation of the pilot unit through 3-way valves (valves V2, V4, V8 and V9 on Fig. 8). The precision on the refrigerant mole fractions is 0.01.

Molar flowrates, have been calculated from the mass flowrates and the composition of the flow. The mass flowrates are obtained by measuring the time for sampling a precise mass of product. The sampling is realized through 3-way valves. The relative error on the molar flowrate is then about 2%.

It is noticeable that temperature T_3 of the vapor cannot be directly measured and is deduced from the measurement of the mole fraction x_3 and VLE.

4. Experimental measurements

4.1. Determination of thermal losses

When feeding the evaporator with pure n-heptane, a part of the produced vapor condense in the column. The measurement of the molar flowrate F_{10} at the bottom outlet allows us to calculate the loss heat flow of the column $Q_{\text{loss COL}}$:

$$Q_{\text{loss COL}} = F_{10} \cdot L_v^{n\text{-heptane}} \tag{2}$$

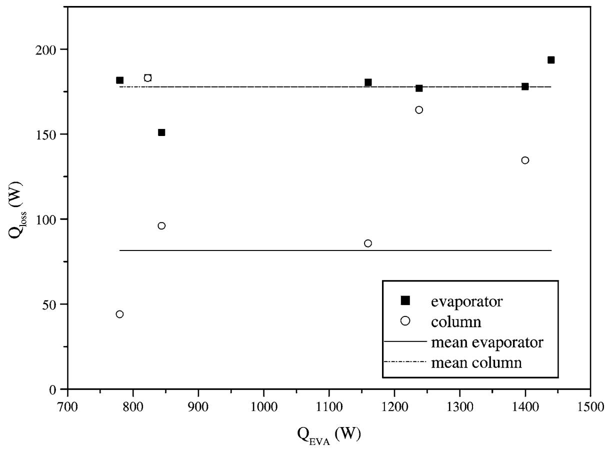

Fig. 9. Thermal losses in the evaporator and the column.

Loss heat flow of the evaporator $Q_{\text{loss EVA}}$ can be calculated by comparing the molar flowrate F_9 of vapor produced if the evaporator was adiabatic, which is deduced from the electrical power supplied to the heating element (Q_{EVA}), and the one experimentally observed which is equal to the sum of the molar flowrates at the bottom and top outlets, F_{10} and F_3:

$$Q_{\text{loss EVA}} = Q_{\text{EVA}} - L_V^{n\text{-heptane}} \cdot (F_{10} + F_3) \qquad (3)$$

Since the results on Fig. 9 are quite dispersed, it is hard to conclude on the dependance of the different thermal losses with Q_{EVA} (Fig. 9). Nevertheless, average values for them can be estimated:

$$Q_{\text{loss COL}} \approx 180\ \text{W}, \qquad Q_{\text{loss EVA}} \approx 80\ \text{W}$$

These values will be used to take into account thermal losses in a simulation code devoted to ADHT cycles. It will also be possible to take into account the dependance of the heat losses with Q_{EVA}.

It is interesting to note that experimental ADHT has been generally operated with a heat supply to the evaporator of 1500 W. The total amount of heat loss represent 17% of the supplied heat. This is one reason for the low value of η_{th} experimentally observed.

4.2. Liquid–liquid phase splitting

It appears that a good phase splitting occurs in the settler. Indeed, for different settler temperatures, mole fraction x_7 and x_1 correspond to the mole fractions of liquid phases in equilibrium (Fig. 10).

4.3. Internal temperature lift—ΔT_i

The internal temperature lift ΔT_i is defined as the difference of temperature between the evaporator outlet (flow 9) and the condenser inlet (flow 3):

$$\Delta T_i = T_3 - T_9 \qquad (4)$$

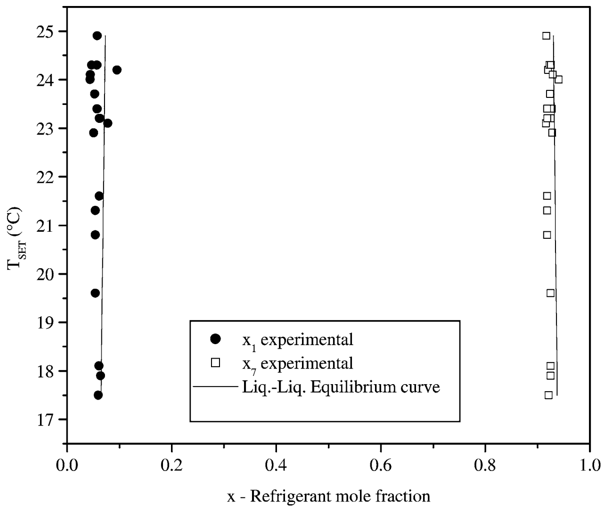

Fig. 10. Phase splitting in the settler.

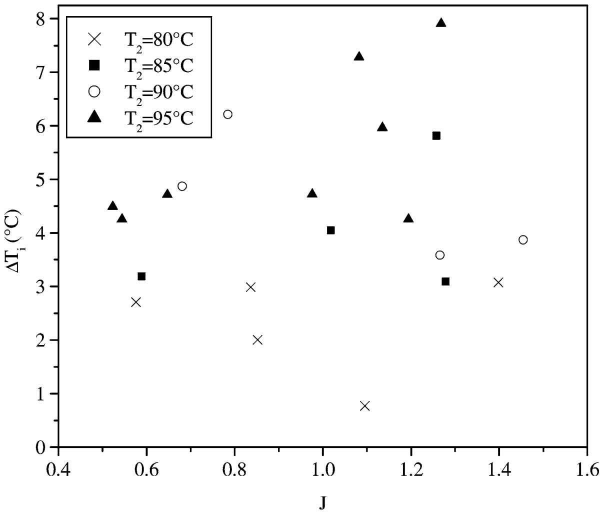

Fig. 11. Influence of J and T_2 on internal temperature lift ΔT_i.

It is a qualitative measurement of the heat upgrading process. In industrial processes, it ranges typically from 30 to 40 °C.

One important operating parameter which influence on ΔT_i has been studied is the molar feed ratio J. It compares the molar flowrates of the inlets of the reverse rectification column:

$$J = \frac{F_2}{F_9} = \frac{F_1}{F_7} \qquad (5)$$

Variations of ΔT_i with J have been studied (Fig. 11). The influence of the preheating of the liquid inlet has also been taken into account by working with different values of T_2.

First, it is important to notice that it has been possible to experimentally upgrade heat with this innovative heat transformer cycle since significant temperature have been observed (up to 8 °C). The practical feasibility of liquid phase separation to replace distillation in absorption heat transformer has consequently been demonstrated.

Off course the observed values of ΔT_i are very low (in most of the case about 4 °C. But, as it has been previously stated, this is due to the choice of the working mixture. Further experimental campaigns, with the use of other working mixtures, will very likely allow to reach industrially meaningful temperature lifts.

It appears that ΔT_i increases with T_2. Indeed, if flow 2 is too cold, an important part of the vapor circulating in the column is used to heat the liquid up to its boiling temperature. So, less vapor will be available for absorption and the height of column devoted to absorption will be reduced. Consequently, the vapor at the top of the column will be poorer in absorbent, which means that T_3 will be lower. This result shows the practical importance of the heat recovery heat exchangers to make the cycle able to reach high temperature lifts.

The study of the influence of J on ΔT_i is more difficult since experimental points are very dispersed. The dispersion of the results is mainly due to experimental uncertainties (on compositions and flowrates) and to the difficulty to operate in a perfect steady state (improvements on the process command seems necessary).

4.4. *Thermal efficiency—η_{th}*

Quantitative performances of the ADHT have been presented using the thermal efficiency, η_{th}:

$$\eta_{th} = \frac{Q_{ABS}}{Q_{EVA}}$$

It is the ratio of the upgraded heat recovered from the condenser to the waste heat supplied to the evaporator. This criterion is generally called coefficient of performance (COP). Nevertheless, this can lead to erroneous conclusions when comparing COP of AHT to COP of compression heat pumps. For compression machines, COP is defined as the ratio of upgraded heat to the mechanical work supplied by the compressor. Hence, COP of CHP are generally superior to 1 whereas COP of AHT are always lower than 1. A fast comparison of these two COP would lead to conclude to the superiority of the CHP. The comparison is not correct since it compares two different criteria. To be exact, the expression of COP for AHT should be written:

$$\mathrm{COP} = \frac{Q_{ABS}}{W_{PUMPS}}$$

Variations of η_{th} with J have been studied (Fig. 12). The influence of the preheating of the liquid inlet has also been taken into account by working with different values of T_2.

It is first interesting to notice that the values of η_{th} experimentally observed vary from 0.3 to 0.4. These results are close to those obtained with conventional AHT. It must be taken into account that the experimental ADHT is absolutely not optimized (no preheating of rich solution, relatively high thermal losses,...). It is therefore possible to expect higher values of η_{th} with a properly designed machine. The thermal efficiency, η_{th}, behave with T_2 in the same way that ΔT_i does. The reason are the same. A too cold liquid inlet in the column leads to condensate a large amount of vapor. The vapor flow rate at the top of the column is then reduced and consequently the upgraded heat recovered in the condenser, Q_{ABS}.

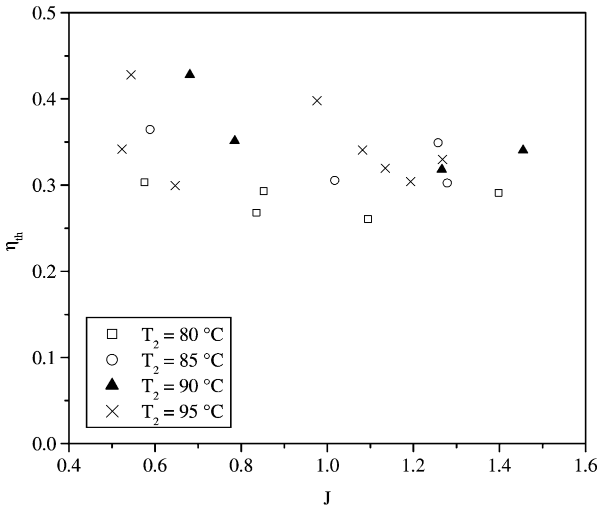

Fig. 12. Influence of J and T_2 on thermal efficiency η_{th}.

It is also difficult to conclude on the influence of J on η_{th} because of the great dispersion of experimental points.

5. Conclusions

Practical feasibility of a heat transformer cycle using a liquid phase separation step, has been clearly demonstrated by the building and operation of an experimental pilot plant using *n*-heptane/DMF as working mixture. Thermal efficiencies similar to those obtained with existing industrial machines have been observed and can be easily increased by optimizing the experimental cycle. The use of an appropriate working mixture will certainly lead to temperature lifts of industrial interest.

References

[1] J. Yin, L. Shi, M.S. Zhu, L.Z. Han, Performance analysis of an absorption heat transformer with different working fluid combination, Appl. Energy 67 (2000) 281–292.
[2] D.A. Reay, D.B.A. Macmichael, Heat Pumps, 2nd Edition, Pergamon Press, New York, 1988.
[3] M. Ishida, J. Ji, Graphical exergy study on single absorption heat transformer, Appl. Thermal Engrg. 19 (1999) 1191–1206.
[4] M. Niang, T. Cachot, P. Le Goff, A new trend in heat recovery from wastes by use of partially miscible working fluids, Energy Convers. Mgmt. 38 (15–17) (1997) 1701–1707.
[5] S. White, B. O'Neill, A novel absorption-cycle heat-pump. Part I: Refrigeration, Appl. Energy 47 (1994) 369–377.
[6] T.K. Sherwood, US Patent 3, 354, 884 (1944).
[7] L.E. Mills, US Patent 2, 638, 760 (1953).
[8] S.M. Walas, Phase Equilibria in Chemical Engineering, Butterworth, London, 1985.
[9] M. Kernen, L.L. Lee, H. Perez-Blanco, A study of solution properties to optimize solution cycle COP, Internat. J. Refrig. 18 (1) (1995) 42–50.

[10] S. White, B. O'Neill, A novel absorption-cycle heat-pump. Part II: Heating, Appl. Energy 47 (1994) 369–377.

[11] D. Alonso, Thermotransformateur à absorption–démixtion : Expérimentation et Optimisation, Ph.D. Thesis, Institut National Polytechnique de Lorraine, France, 2000.

[12] D. Alonso, T. Cachot, J.M. Hornut, Performance simulation of an absorption heat transformer operating with partially miscible mixtures, Appl. Energy, to be published.

[13] P.M. Ranger, H. Matsuda, P. Le Goff, Modeling of a new type of absorption heat-pump combining rectification and "reverse rectification", J. Chem. Engrg. Japan 23 (5) (1990) 530–536.

[14] K. Quitzsch, D. Strittmatter, G. Geiseler, Studien zur thermodynamik binärer flüssigkeitgemische mit homologen formamiden, Z. Phys. Chem. 240 (1969) 107–126.

[15] T. Zemlyanskaya, F. Komarova, L. Kormina, Y. Garber, Liquid–vapor equilibria in binary system, J. Appl. Chem. USSR 50 (1977) 1116–1117.