



Quest for an efficient binary working mixture for an absorption-demixing heat transformer



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ABSTRACT

The aim of the present paper is to identify a highly efficient binary mixture to be used in an absorption-demixing heat transformer (ADHT) in order to make it more energy-efficient than the conventional absorption heat transformer (AHT). Firstly, 128 binary mixtures potentially interesting in terms of pure component boiling temperatures and upper critical solution temperature (UCST) were selected among thousands for which experimental information related to partial miscibility was available. Secondly, the parameters of the NRTL activity coefficient model were determined for each selected mixture, showing a good agreement between phase-equilibrium calculation and experimental data points. Hence, with the help of the reliable NRTL model, the performance evaluation of the ADHT cycle operating with various working pairs was carried out through the estimation of the internal temperature lift (ΔT_i). Despite a large number of binary mixtures investigated, only 38 ones showed a positive ΔT_i and the most significant value was about 5 K. Finally, in the light of the undertaken modeling work, it was possible to establish the characteristics of the best binary mixture usable in an ADHT. Consequently, a highly efficient binary mixture exhibiting a ΔT_i value of 50 K for industrial application certainly does not exist, owing to the conflict among its characteristic requirements.

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1. Introduction

Taking account of the environmental regulations and the energy efficiency, a suitable heat transformer can be a technological solution for storing, recovering and upgrading industrial waste heat, so as to reduce gas emissions, improve process efficiency and limit the use of ground water for cooling.

In recent years, absorption heat-transformers (AHT) were largely investigated by researchers in order to improve their performance [1–4]: novel cycles [5–9] were invented; new working pairs were selected [10–16]. Although the AHT cycle has currently a considerable interest in industrial applications [17–22], the widely used water + lithium bromide [23–26] working mixture suffers of severe limitations. It is indeed limited by corrosion at high temperatures and by crystallization at high concentrations of LiBr. The solid–liquid phase diagram of such a system highlights that crystals of pure LiBr may appear during the cooling of a liquid H₂O + LiBr solution. As an example if the LiBr content is about 65%, the crystallization danger appears at 45 °C and this crystallization temperature increases when the LiBr content increases. The major

drawbacks of such processes are the loss of exergy and the cost of the purification step. In order to overcome the limitations inherent in the AHT, several authors [27–29] suggested to use partially miscible working pairs in an absorption-demixing heat transformer (ADHT), where only a simple decanter – instead of a distillation column – is used to dissociate the mixture. The ADHT cycle is very promising not only for the primary energy saving but also for the investment-cost saving. For organic Rankine cycles, many working fluids were tested [30,31] but to our knowledge, the performance of a ADHT cycle was only determined for four different working pairs [28,29,32–34]: water + furfural, *n*-heptane + *N,N*-dimethylformamide (DMF), cyclohexane + dimethylsulfoxide (DMSO), cyclohexane + aniline. For the water + furfural system, Niang et al. [28] and Kottenko et al. [34] calculated a COP of 0.86 for a temperature lift of 25 K. According to White and O'Neill [29], the cyclohexane + aniline working pair leads to poor thermodynamic performance. Alonso et al. [32,33] calculated a small temperature lift (10 K) but a relatively high COP of 0.93 for the *n*-heptane + DMF system. The same authors were however able to obtain a higher COP (0.96) and a larger temperature lift (close to 50 K) for the cyclohexane + DMSO system. Alonso et al. [32] however explain that the latter working pair can not be used to thermally upgrade heat flows from 50 to 90 °C as done in traditional AHT thus seriously limiting the potential use of such a system. Such a working

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pair can indeed only upgrade waste heat flows which are initially hot (e.g. from 125 to 175 °C).

The aim of the present work is to test hundreds of binary systems in order to possibly identify a highly efficient working pair for a ADHT cycle so that a temperature lift of 30 K (ideally, 50 K for industrial application) could be obtained on waste heat flows available at around 50 °C.

2. ADHT cycle description

An absorption-demixing heat transformer (ADHT) is shown schematically in Fig. 1. The working fluid is a binary mixture exhibiting a miscibility gap at low temperature. Note that the most volatile component is classically called *refrigerant*. In the generator, two liquid phases of different compositions are in equilibrium. The refrigerant-rich liquid phase is noted RD and the other one – poorer in refrigerant – is noted PD. RD is then completely vaporized in the evaporator receiving the waste heat Q_{eva} , and becomes a vapor (R_1). In the reverse rectification column, the refrigerant-poor liquid phase (PD) arriving at the top is mixed with the vapor phase (R_1) entering at the bottom. The vapor (R_2) leaving the top of the column is then condensed to its bubble-point (CO) in the condenser and heat at a high temperature level Q_{con} can be recovered. The mixture (M') issued from the mixing of the two liquid phases (CO and P_2) exiting respectively the condenser and the bottom of the reverse rectification column is fed to the generator to start a new cycle. The low temperature heat Q_{gen} is extracted from the generator at a specified temperature. The ADHT cycle is isobaric and generally works under atmospheric pressure.

The main purpose of an ADHT cycle is to produce useful heat Q_{con} at a high temperature level by using waste heat Q_{eva} at a medium temperature level. As shown in Fig. 1, the hot gaseous stream (R_1) and the cold liquid stream (PD) are mixed in the reverse rectification column to generate the gaseous stream (R_2) at high temperature. In order to evaluate the performance of the ADHT cycle, the internal temperature lift (ΔT_i) defined as the temperature difference between streams R_2 and R_1 is considered in this study:

$$\Delta T_i = T_{R_2} - T_{R_1} \quad (1)$$

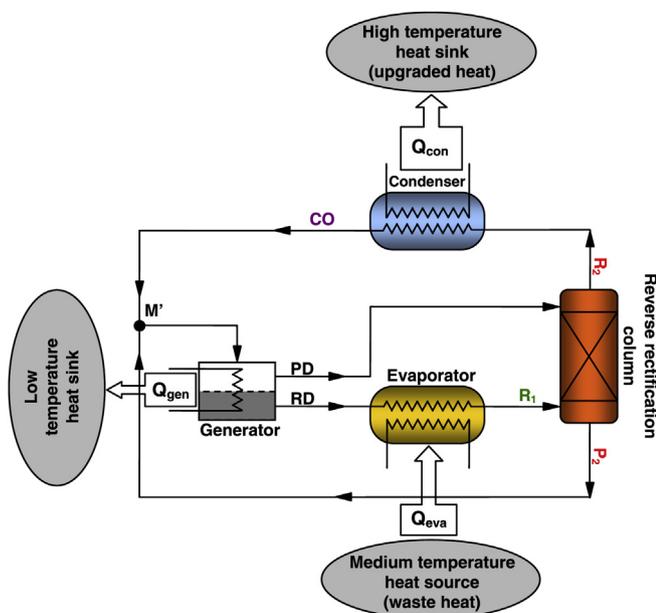


Fig. 1. Process diagram of a conventional absorption-demixing heat transformer (ADHT).

As pointed out by several authors [32,33,35], ΔT_i is an important performance criterion for the ADHT cycle, quantifying heat upgrading from medium to high temperature. It is important to note that the proposed definition of ΔT_i maximizes the temperature lift value since during condensation, the temperature drops from T_{R2} (dew temperature) to T_{CO} (bubble temperature). Hence, upgraded heat is not entirely released at the highest temperature. As highlighted by Kottenko et al. [34], the outlet condenser temperature can even be very close to the evaporator temperature (about 1 K for a water/furfural mixture). This can constitute – for practical applications – a serious drawback of such a cycle.

The two hypotheses made to simulate the conventional ADHT cycle are detailed in the two next subsections and are illustrated using appropriate isobaric phase diagrams. Several choice criteria aimed at selecting an efficient binary mixture are then discussed in a third subsection. Finally, in a fourth subsection, the behavior of azeotropic mixtures which are largely met in this study is analyzed.

2.1. First hypothesis

The reverse rectification column in Fig. 1 is replaced by a flash drum (single equilibrium stage) as shown in Fig. 2.

Although this simplification grandly helps the identification procedure of an efficient working mixture, the ADHT cycle performance is then remarkably decreased by this modification. This hypothesis however does not impact the purpose of this work (which is to identify a highly efficient working pair among various binary mixtures) since the best pair for a cycle using a reverse rectification column remains the best pair for a cycle involving a single flash drum. Fig. 3a shows the isobaric temperature–composition (T – xy) phase diagram of a fictitious binary system. The solid black lines demarcate the liquid–liquid and vapor–liquid phase–equilibrium regions at low and high temperatures, respectively. The corresponding isobaric enthalpy–composition (h – xy) phase diagram, shown in Fig. 3b, is convenient to understand the path followed by the fluid in the ADHT cycle since in contrast to the T – xy plane, it becomes possible to draw the operating line [R_1 PD], the equation of which comes from the combination of energy and mass balances applied to the flash drum. The solid black lines mark again the boundaries of the liquid–liquid and vapor–liquid phase–equilibrium regions, whereas isotherms are represented with

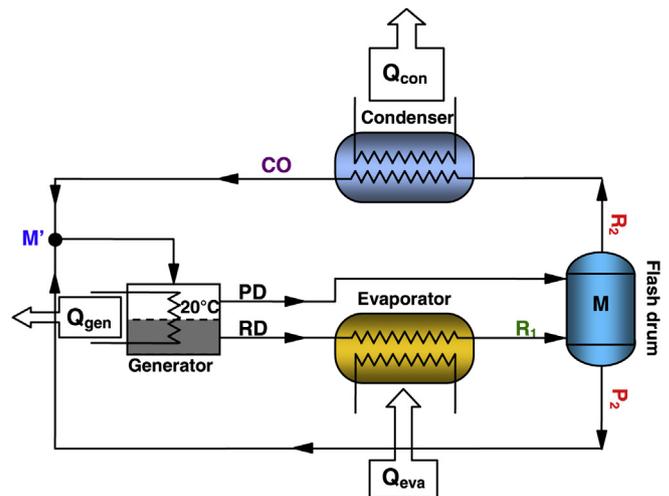


Fig. 2. Process diagram of a simplified ADHT cycle in which the reverse rectification column is replaced by a flash drum thus illustrating the first hypothesis of our simulations.

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